Chapter 6

Assessment of Cement Raw Materials

ASSESSMENT OF CEMENT RAW MATERIALS

1. ASSESSMENT OF CEMENT RAW MATERIALS

1.1 Definition of qualitative requirements of clinker and cement

Ordinary Portland Cement (OPC) - by far the most frequently used type of cement -consists mainly of the four major chemical components:

Calcium oxide	64 % CaO	"Lime", Calcium, C
Silicon oxide	22 % SiO_2	"Silica", S
Aluminium oxide	6 % Al_2O_3	"Alumina", A
Iron oxide	3 % Fe_2O_3	"Iron", F

The remainder is composed of:

Na_2O, K_2O	"Alkali"
SO_3	"Sulphur"
MgO	"Magnesium
TiO_2	"Titanium"
etc.	

It should be noted that nature only seldomly provides a raw material of the desired chemical composition. Normally, mixtures of various components are necessary to obtain the raw mix suitable for the production of OPC.

1.2 Raw materials for the cement industry

1.2.1 General

Basically, the following raw material classes can be distinguished:

◆ **Main components**
They contribute CaO, SiO_2, Al_2O_3 and Fe_2O_3. CaO is supplied by the calcareous (carbonatic) component

and

SiO_2 Al_2O_3 and Fe_2O_3 by the argillaceous (siliceous) component (s).

◆ **Corrective Materials**
If there is a deficiency of either CaO, SiO_2, Al_2O_3 or Fe_2O_3, respective "corrective" Materials providing the deficient component(s), have to be utilised.

◆ **Additive Materials**
Materials which are added to the raw mix (i.e. to the mix consisting of main components and possibly corrective Materials or to the clinker in order to obtain special effects, are designated as "additive" Materials.

1.2.2 Calcareous Component

As demonstrated in chapter 1.3, the calcareous component is usually classified according to its chemical Composition i.e. according to its carbonate content ("titration value").

The carbonate content - expressed as $CaCO_3$ content is normally higher than 75 %, the sought after $CaCO_3$ content of the cement raw mix.

The following classification system is employed in the cement industry (Table 19):

Table 19 **Classification of calcareous rock (according to chemical composition)**

% $CaCO_3$	Designation
95 - 100	high-grade limestone
85 - 95	limestone
75 - 85	marly limestone

However, by applying only chemical Information nothing is stated regarding the appearance, lithology, type of formation, etc. of such rocks. A great variety of rocks may fulfill the above classification (refer Table 20).

Table 20 **Calcareous cement raw Materials**

"limestone" marly limestone chalk coral limestone marble "lime-sand" shell deposits etc.

The above can all have an identical titration value!

According to specifications for a cement raw mix, a perfectly suited raw material would contain approx. 75 % $CaCO_3$ and 25 % clay and sand components. Such raw Materials very seldom occur in nature as e.g. natural cement stone".

The economic value of a Potential industrially processed cement raw material depends largely on its conformity with the above specifications, i.e. conformity means favourable economy. It is wrong to assume that an increased carbonate content of a calcareous raw material would result in a higher economic value. For example, a calcareous component with 80 - 85 % $CaCO_3$ is often preferable to a high-grade limestone with 95 - 100 % $CaCO_3$ because fewer other raw Materials have to be added to meet the specifications.

Note
It should be pointed out that the titration method for the carbonate determination includes all carbonates, i.e. the "titration value" is not identical with the $CaCO_3$-content but includes $MgCO_3$, $FeCO_3$, Na_2CO_3, etc.
Titration thus produces only guide values which have to be verified by means of total chemical analysis.

1.2.3 Argillaceous Component

The term "argillaceous" covers the field of cement raw materials with those chemical constituents which are contained in insufficient quantities in the calcareous component, i.e. argillaceous materials basically supply SiO_2, Al_2O_3 and Fe_2O_3 ("silica", "alumina" and "iron").

Because of the various mechanisms in the formation of argillaceous rock, a large number of these rock types are considered as potential cement raw materials (Table 21).

Table 21   Argillaceous materials

clay	"clay" loess	unconsolidated, loose
	claystone mudstone siltstone (slate) shale	consolidated, compact
marl	calcareous marl marl clayey marl marly clay	CaCO₃ 65 - 75 % 35 - 65 % 25 - 35 % 15 - 25 %
others	tuff ash phyllite slate amphibolite	volcanic origin metamorphic origin

1.2.4 Corrective Materials

If the main components (calcareous and argillaceous component) do not permit the proportioning of a mix which conforms to the specifications, corrective materials have to be utilised.

Contrary to the main components, the concentration of the desired constituent (SiO_2, Al_2O_3 or Fe_2O_3) in the corrective is of utmost importance. Since corrective Materials (Table 22) are usually expensive (bought from special suppliers) and occasionally have to be transported over long distances, the corrective should be of high quality and used in small quantities.

Table 22   corrective Materials

To correct the deficiency of	corrective material	minimum concentration
"iron" (Fe_2O_3)	Iron ore Pyrites ash	60% Fe_2O_3 60% -90%
"alumina" (Al_2O_3)	Bauxite Laterite Kaolinite	50% Al_2O_3 25% " 50%
"silica" (SiO_2)	Quartzsand Quartzite	80% SiO_2 80% "
"lime" (CaO)	Limestone Marble	90% $CaCO_3$

In rare cases, where the abundant calcareous materials do not contain a sufficient amount of calcium carbonate, a high-grade limestone (CaO) - corrective has to be supplied.

1.2.5 Additive Materials

Additive materials (Table 23) include, in most cases, only sulphate-bearing components which are added to the clinker by inter-grinding for control of the setting of cement. In earlier times, another additive material (fluorspar) was frequently added to the kiln feed in order to improve the burnability. Today, it is only employed in very rare cases (manufacture of white cement).

A great variety of special cements is produced by blending OPC with either waste or by-products of other industries (steel industry, power plants) or with naturally occurring materials, yielding latent hydraulic properties (pozzolana).

Table 23 Additive materials

Additive	minimum concentration	purpose of addition
Gypsum $CaSO_4 . 2 H_2O$ Anhydrite $CaSO_4$	35% SO_3 50% SO_3	production of OPC (95% clinker + 5% gypsum)
Fluorspar	30% F	improvement of burnability
Blastfurnace slag Pozzolana Fly ash	none	special cements

1.2.6 Combination of Components

Criteria for the selection and combination of raw material components are:

♦ chemical composition
   (overall, homogeneity, variability, etc.)

♦ technological properties

♦ Transport and costs

♦ material casts

♦ operation (handling, preparation, etc.)

Basically, it is desirable to reduce the number of components to a minimum - taking of course the above i.e. two-component mixes instead of three or four component mixes. For instance:

limestone clay	instead of	limestone sand iron ore bauxite
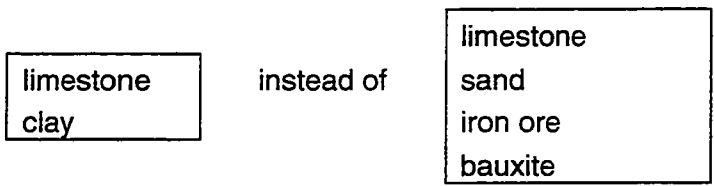
Potential cement raw mixes with a large number of components (more than three or four) may be subject to difficulties regarding dosage, control of components and of cement raw mixes, etc. Industrially produced cement raw mixes are compiled in Table 24.

**Table 24   Examples of combinations of components
("Holderbank"-Group plants)**

Mississauga	Guayaquil
98 - 100 % marly limestone	82 - 85 % limestone
0 - 2 % shale	12 - 15 % clay
	1 - 3 % iron ore
Apasco	
77 - 85 % limestone	**Geelong**
8 - 22 % clay	55 % high-grade "limestone
0 - 4% sandy clay	44 % low-grade "limestone"
1 -3 % iron ore	
Atocongo	1% pyrites ash
27 % limestone	
73 % marl	**Hardegsen**
	92 % limestone
Darra	7 % sand
91 % coral	0.5 % iron ore
5 % sand	0.5 % gypsum (SO$_3$)
3 % clay	
1 % iron ore	**Obourg**
Dudfield	89 % limestone
88 % limestone	6 % sandy marl
6 % clay	1 % pyrites ash (Fe$_2$O$_3$)
6 % boiler ash (Al$_2$O$_3$)	1 % coal mine waste
0 - 1 % magnetite (Fe$_2$O$_3$)	3 % coal mine waste
pyrites ash (Fe$_2$O$_3$)	containing combustibles
Wunstorf	**Gmunden**
91 % limestone / marl	68 % limestone
1.5 % clay	29 % marl
4.54 % sand	3 % iron oxide
3 % iron ore	

1.3   Characteristics of cement raw material

1.3.1   Chemical Characteristics

Any assessment of potential cement raw Materials is predominantly based on their chemical composition The following system (Table 25) for the presentation of chemical results has been developed:

Table 25   Form for presentation of chemical results

Constituents	Designation
* SiO_2 AL_2O_3 Fe_2O_3 CaO	"main elements" (oxides)
MgO SO_3 K_2O Na_2O	"minor elements"
TiO_2 Cr_2O_3 Mn_2O_3 P_2O_5 Cl F	"Trace elements"

* plus loss on ignition

It should be mentioned that the assessment of each raw material component has to be made with consideration of a potential raw material combination; i.e. it should not be assessed in isolation but take into account the other components involved and the specifications for the cement raw mix.

For example:

A limestone yielding 98 % carbonate content may contain 3.5% MgO. An isolated assessment would result in the rejection of this Materials If the raw mix consists of 20 % clay (say without MgO) and 80% limestone to achieve a carbonate content of 75%, a MgO content of approx. 2.8% (4.5 % resp. when loss on ignition free) results, which is still tolerable for most markets.

The following tables (26 - 30) display a series of analytical results of cement raw materials and are to be interpreted according to the above criteria.

Table 26 **Analyses of calcareous cement raw materials**

Designation	lime-stone	high-grade limestone	chalk	sandy limestone	marble	calcareous marl	phosphatic limestone	dolomitic limestone	dolomite
Ignition loss	42,90	42,90	42,26	35,23	43,14	30,60	42,0	37,5	45,63
SiO_2	5,19	0,70	2,38	15,74	1,10	13,80	2,0	16,7	3,24
Al_2O_3	0,81	0,68	1,57	0,88	0,51	7,00	0,37	2,1	0,17
Fe_2O_3	0,54	0,08	0,56	0,51	0,25	4,55	0,56	0,27	0,27
CaO	48,61	54,54	52,48	44,89	54,33	38,35	52,1	33,6	29,58
MgO	1,90	0,59	0,59	2,54	0,48	1,32	0,76	9,3	20,84
SO_3	0,05	0,25	0,01	0,61	0,04	0,43	0,23	0,08	0,02
K_2O	0,33	0,01	0,02	0,21	0,01	0,86	0,08	0,29	0,11
Na_2O	0,05	0,16	0,02	0,08	0,01	2,61	0,36	0,40	0,02
TiO_2	0,06	0,01	0,01	0,05	0,02	0,21	0,01	0,07	0,01
Cr_2O_3	0,01	0,01	0,01	0,01	0,01	0,02	0,01	0,01	0,01
Mn_2O_3	0,05	0,01	0,01	0,03	0,08	0,29	0,06	0,06	0,01
P_2O_5	0,04	0,01	0,01	0,10	0,03	0,25	0,98	0,20	0,02
Cl	0,02	0,01	0,03	0,11	0,01	0,04	0,04	0,12	0,03
F	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01
Total	100,11	99,97	99,97	101,00	100,16	100,34	99,57	100,71	100,97

Theoretical composition of dolomite:

MgO 21.9 %, CaO 30.4 %, CO_2 47.7 %

Table 27 **Rock Analysis of argillaceous cement raw materials**

Designation	Shale	Shale	Marl	Claystone	Clay	Calcareous sandstone	Sandy shale	"Slate"	"Cement-stone"
Ignition loss	3,71	5,3	32,24	13,3	12,50	23,8	3,9	5,58	34,44
SiO_2	61,1	64,1	22,7	48,6	45,90	46,3	70,8	56,29	11,2
Al_2O_3	16,4	13,6	3,9	19,6	23,90	1,2	10,9	19,22	4,02
Fe_2O_3	7,1	6,1	2,4	9,1	15,50	0,64	5,2	4,39	1,68
CaO	1,1	1,8	32,9	2,5	0,72	28,1	1,3	0,09	44,01
MgO	2,4	2,9	3,32	1,6	0,33	0,48	2,2	1,65	1,30
SO_3	0,01	0,03	0,95	1,78	0,03	0,04	0,03	0,72	0,13
K_2O	4,8	2,7	0,59	0,54	0,01	0,06	2,2	10,85	0,96
Na_2O	1,6	1,9	0,19	1,00	0,11	0,10	2,0	0,19	0,42
TiO_2	0,76	0,67	0,39	1,20	0,86	0,06	0,71	0,64	0,68
Cr_2O_3	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,02
Mn_2O_3	0,06	0,05	0,04	0,04	0,20	0,04	0,05	0,22	0,45
P_2O_5	0,13	0,18	0,93	0,18	0,06	0,03	0,17	0,15	0,12
Cl	0,02	0,01	0,01	0,22	0,04	0,03	0,01	0,06	0,04
F	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01
Total	99,21	99,36	99,68	99,68	99,88	100,80	94,49	100,07	99,53
Igneous and metamorphic equivalents	Granite, Rhyolithe Quartzdiorite Gneiss		Calcsili-cate fels	Diorite, Basalts Andesite Gneiss		Calcsili-cate fels	Granite Gneiss	Syenite Trachite Calcsili-cate fels	Sili-ceous marble

Table 28 Analysis of corrective materials

Corrective for	Aluminium			Iron				Silicon	
Designation	Bauxite	Bauxite	Bauxite	Pyrites ash	Hema-tite	Umber	Iron slag	Sand	Sandstone
Ignition loss	10,5	29,35	15,4	n.d.	3,41	13,99	1,6	0,91	3,69
SiO_2	4,3	3,3	3,1	7,8	11,0	32,1	21,5	94,70	80,2
Al_2O_3	56,0	56,6	57,6	1,0	3,1	4,3	8,8	2,90	8,37
Fe_2O_3	22,1	9,4	15,8	84,3	77,7	37,5	57,6	0,24	3,26
CaO	n.d.	1,15	4,1	0,8	1,2	1,42	3,1	0,35	3,29
MgO	n.d.	0,08	0,16	0,45	0,32	1,70	3,6	0,13	0,45
SO_3	n.d.	0,24	0,29	11,73	2,10	0,04	2,3	0,01	0,08
K_2O	n.d.	0,15	0,08	0,09	0,48	0,69	n.d.	1,3	1,90
Na_2O	n.d.	0,10	0,08	0,07	0,07	0,30	n.d.	0,20	0,11
TiO_2	3,0	n.d.	2,9	0,16	0,19	3,24	n.d.	0,12	0,48
Cr_2O_3	n.d.	n.d.	0,02	n.d.	0,01	0,24	n.d.	0,01	0,01
Mn_2O_3	n.d.	n.d.	0,03	0,04	1,31	5,75	n.d.	0,03	0,01
P_2O_5	n.d.	n.d.	0,21	n.d.	0,02	0,16	n.d.	0,01	0,02
Cl	n.d.	n.d.	0,01	n.d.	0,02	0,08.	n.d.	0,01	0,01
F	n.d.	n.d.	0,01	n.d.	0,01	0,02	n.d.	0,01	0,01
Total	n.d.	100,37	99,79	n.d.	100,94	101,53	98,50	100,93	98,89

Table 29   Analysis of attitive materials

Design.	Gypsum	Gypsum	An-hydrite	Fluor-spar	Pozzo-lana	Fly ash	Blast fur-nace slag
L.o.i.	22.3	12.8	0.3	4.6	8.8	1.5	0.18
SiO_2	1.3	9.2	4.8	9.2	54.1	50.1	36.3
Al_2O_3	0.71	2.6	2.6	0.73	17.1	29.0	9.2
Fe_2O_3	0.3	0.95	2.1	1.8	5.5	7.9	0.2
CaO	30.6	30.3	36.2	ca.39.9	4.1	4.5	32.9
MgO	0.05	0.5	2.5	0.11	1.6	2.2	10.4
SO_3	45.5	37.2	51.3	3.1	0.15	0.24	3.4
K_2O	0.08	1.18	0.10	0.26	5.1	2.6	1.3
Na_2O	0.2	0.97	0.02	0.14	2.3	0.37	0.3
TiO_2	0.01	0.88	0.01	0.26	0.78	0.91	0.3
Cr_2O_3	0.01	0.16	0.01	n.d.	0.01	0.02	0.01
Mn_2O_3	n.d.	0.64	0.02	0.02	0.14	0.05	1.5
P_2O_5	n.d.	1.52	0.12	0.05	0.22	0.16	0.01
Cl	n.d.	0.16	0.02	n.d.	0.04	0.01	0.01
F	n.d.	0.35	0.01	37.8	0.01	0.01	0.01
Total	101.06	99.61	100.11	97.99	99.95	99.47	96.13

Theoretical composition of pure gypsum $(CaSO_4 . 2H_2O)$

SO_3	= 46.5 %
CaO	= 32.5 %
H_2O	= 21.0 %

Theoretical composition of pure anhydrite $(CaSO_4)$

SO_4	= 58.8 %
CaO	= 41.2 %

Theoretical composition of fluorspar (CaF_2)

F	= 48.7 %
Ca	= 51.3 %

Carbon not included

Table 30   Typical analyses of cement raw materials

n.loss	3.01	19.17	3.21	8.05	26.89	42.56	41.35	15.4	1.9	13.45
O₂	78,70	43,28	66,55	58,11	27,86	1,65	8,36	3,1	3,4	48,15
₂O₃	7,53	9,31	16,93	15,40	3,64	0,45	1,77	57,6	0,91	12,6
₂O₃	4,57	3,90	3,89	6,47	1,54	0,02	1,08	15,8	90,0	5,2
O	1,29	17,55	1,07	3,10	31,39	54,23	29,03	4,1	0,66	10,15
O	1,32	1,62	0,96	2,44	4,44	0,11	16,68	0,16	0,20	5,25
₃	0,03	0,02	0,26	0,65	0,09	0,06	0,14	0,29	1,5	0,45
O	2,24	2,40	3,60	3,24	2,48	0,36	1,08	0,08	0,15	2,5
₂O	1,14	1,22	2,05	1,30	0,78	0,28	0,06	0,04	0,09	1,03
O₂	0,51	0,68	0,80	0,65	0,20	0,04	0,01	2,9	0,10	0,61
₂O₃	0,02	0,02	0,01	0,02	0,02	0,01	0,01	0,03	0,03	0,01
₂O₃	0,08	0,11	0,04	0,16	0,02	0,02	0,03	0,03	0,03	0,07
₂O₅	0,09	0,75	0,45	0,17	0,20	0,05	0,06	0,17	0,05	0,14
l	0,06	0,01	0,04	0,08	0,06	0,02	0,01	0,01	0,01	0,01
	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01
otal	100,60	100,05	99,87	100,30	99,62	99,87	99,68	99,72	99,04	99,63

1.3.2   Crystallographic Characteristics

1.3.2.1   The Crystalline and Amorphous State

Most materials, e.g. rocks and soil, metals and alloys, concrete and organic substances, are "crystalline", i.e. the atoms, ions and-molecules which form the crystals are arranged in strict geometrical order.

"Amorphous" solids on the contrary are substances with no strict geometrical order, i.e. which are not "crystalline". Glasses and certain resins belong to this class.

1.3.2.2   Definition of a Crystal

Crystals are chemically and physically homogeneous, regularly shamed polyhedral bodies.

1.3.2.3   Space Lattice and Unit Cell

Geometrically, a space lattice (Fig. 33) is defined as a regular and unlimited Arrangement of identical points in space. The lattice of a crystal is merely the repetition in three dimensions of the positions occupied by its atoms or molecules. As Fig. 33 shows, a crystal is built up of a multitude of "unit cells" having edges a_0, b_0, c_0 and angles, α, β, δ,. The length of the edges, called lattice constants, is of the order of a fraction of a nanometer (1 nm = 10^{-9} m; equivalent to 10 Ångströms as an old unit).

The unit cell may be a regular cube, a prism, a rhombohedron or, generally, a parallel epipedon. The lattice constants a_0, b_0. and c. may be equal to one another or different, as may also the angles α, β, δ,., According to the combination, seven different crystal systems occur which are summarised in Table 31.
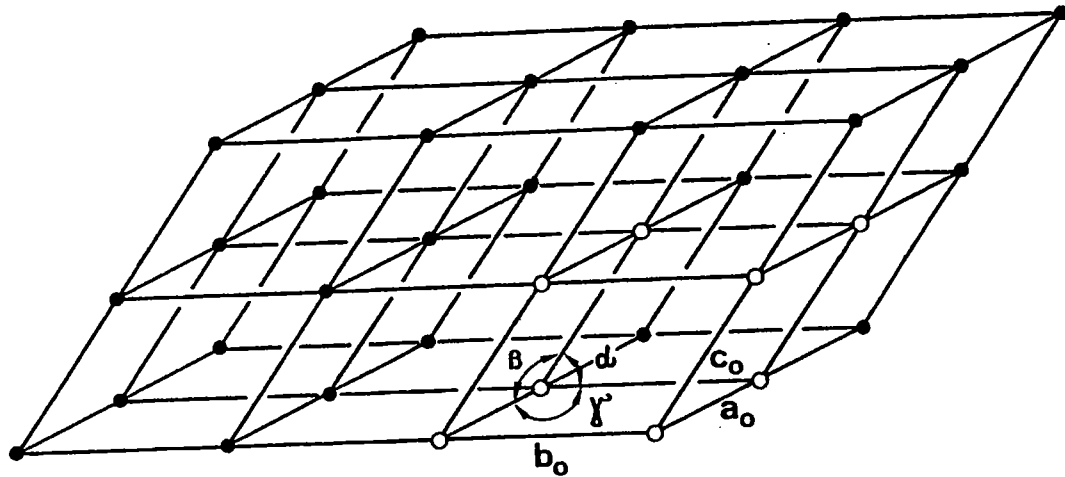
Fig. 33   Crystal lattice


Table 31   Definition of crystal symmetry systems

System	Axial relationships	Angles between crystal axes
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° ; \beta \neq 90°$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Trigonal (Rhombohedral)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Hexagonal	$a_1 = a_2 = a_3 \neq c$	$\alpha_1 = \alpha_2 = \alpha_3 = 120°; \gamma = 90°$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Cubic (isometric)	$a = b = c$	$\alpha = \beta = \gamma = 90°$

According to the positions of atoms, ions and molecules (on the edges or on the faces or in the centre of the unit cell) fourteen space lattices are possible (Fig. 34). Every crystal belongs to one of these crystal systems and is composed of an infinite repetition in the three dimensions by one of the 14 space lattices.

A simpler presentation and characterisation of the point lattice is achieved by the introduction of "lattice planes". Equispaced planes, i.e. parallel planes with same distance represent identical two-dimensional arrangements of atoms and molecules (Fig. 33).

Fig. 34   **Space lattice**
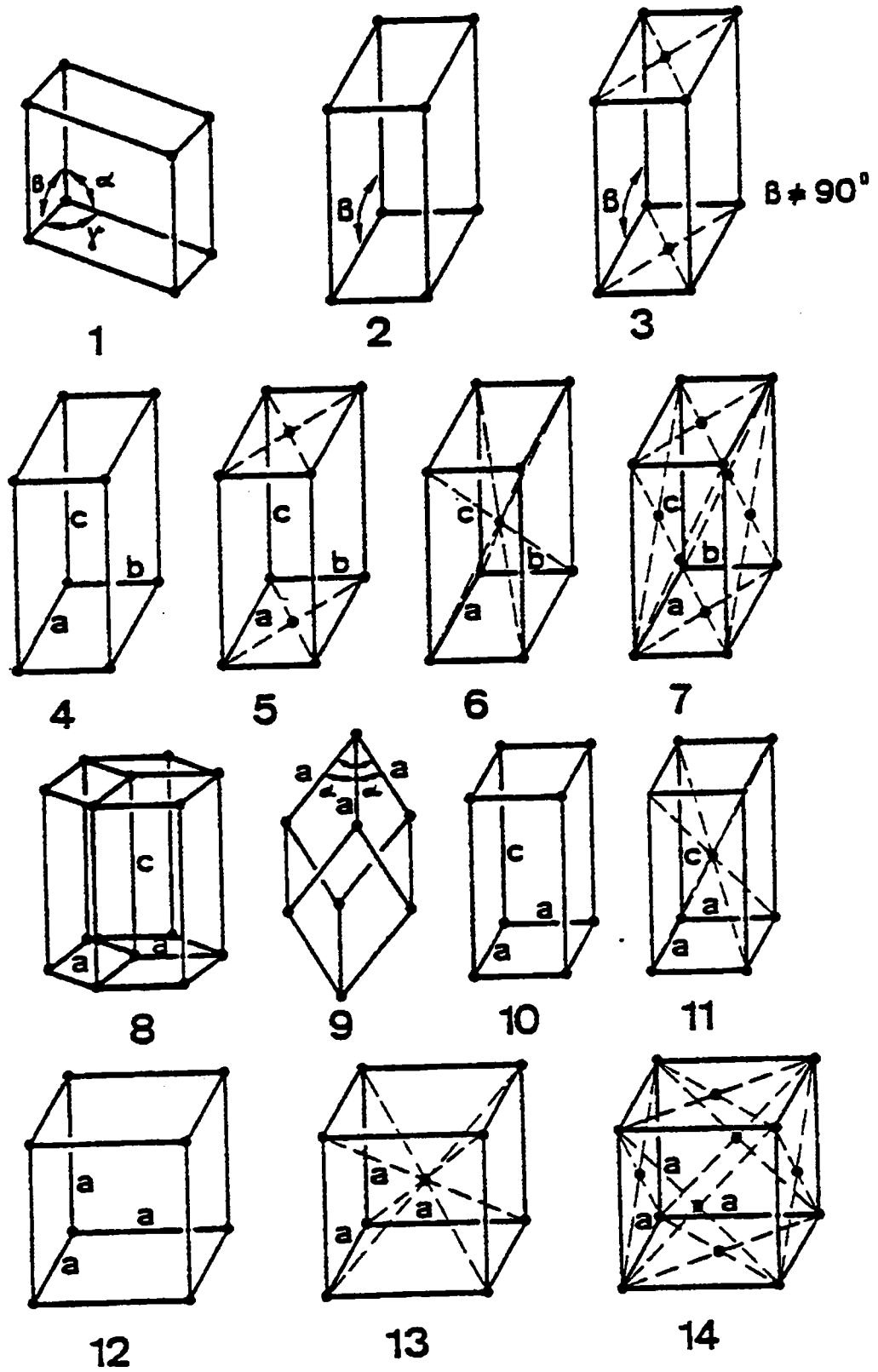
1.3.2.4 Symmetry Elements of Crystals and Crystal Symmetry Classes

Symmetry is an essential feature of crystals. The symmetry elements are simple and few in number, viz. axes, planes and centre of symmetry.

The symmetry properties of all crystals are combinations of these axes, planes and centre of symmetry. The total number of possible combinations of symmetry elements leads to 32 crystal symmetry classes.

1.3.2.5 Definition of Minerals

A mineral is defined as a solid characterised by its chemical composition and crystal structure (lattice constants and symmetry).

1.3.2.6 Ray Diffraction for Determination of Crystal Structure and Identification of Minerals

X-ray diffraction is a tool to supply data and information on the crystal structure not obtainable by other techniques. In the cement industry it is applied for the identification of the mineralogical composition of raw Materials clinker, rings, refractory Materials cement and hydration products. It is based on the determination of the distance "d" between equispaced planes of the crystal lattice (4.3.2.3). A set of characteristic d - values represent the "fingerprint" of a mineral.

When a monochromatic beam of X-rays of wavelength (X of the same order of magnitude as the distance between lattice points) falls on a crystal, the characteristic fingerprint of the corresponding mineral is produced by reflection. This phenomenon is not a surface reflection as with ordinary light. Rather it can be compared with the diffraction of a monochromatic light-beam on an optical lattice. This phenomenon normally called "X-ray diffraction" is explained as follows (Fig. 35):

Parallel to the crystal face is an infinite series of equispaced atomic planes, spaced at a distance d. The X-rays penetrate to a depth of several million of such planes, whereby they may undergo the same reflection as on the surface plane. If these various reflections arrive in phase, they form a composite reflected X-ray beam. If the reflection on the multitude of identical planes occurs out of phase, the X-ray in the crystal is absorbed and no reflection occurs.

Fig. 35   Reflection of X-rays on atomic planes
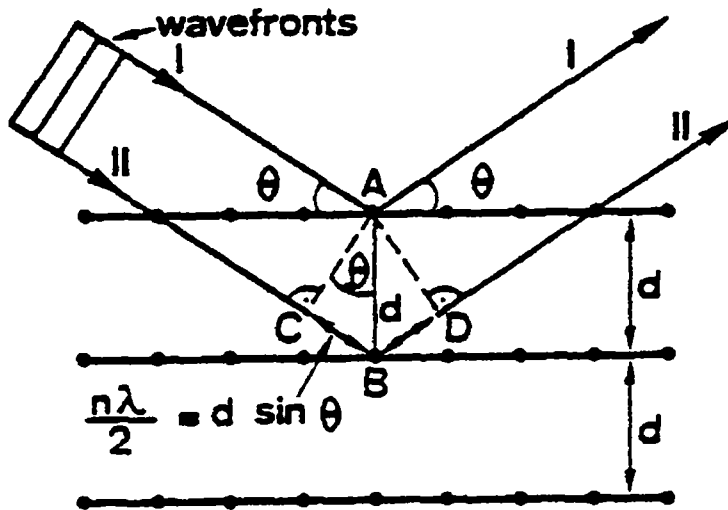
θ ■ incident angle of the X—Ray beam

d ■ distance between the parallel atomic planes

λ ■ wavelength of the monochromatic X—Ray beam

Geometrical considerations (Fig. 35) demonstrate that reflection occurs only under the following, so-called Bragg conditions:

$$n \lambda = 2d \sin \theta \quad \text{or} \quad d = \frac{n\lambda}{2\sin\theta}$$

n = integer, order of diffraction

For the practical application in the cement industry, x-ray diffraction analysis is carried out on finely ground samples ("powder method"). This means that with in the powder sample an infinite number of minute crystals is randomly distributed and oriented. Therefore, all possible series of equispaced identical lattice planes with all the different d values are recorded.

Fig. 36 shows in a schematic way the principle of powder-x-ray diffractometry from which an x-ray diffraction diagram results (Fig. 37).

Fig. 36   Diffractometer (Goniometer type)

Counter tube

θ A θ 2θ

Sample holder with
fine powdered sample

A = axis of the goniometer
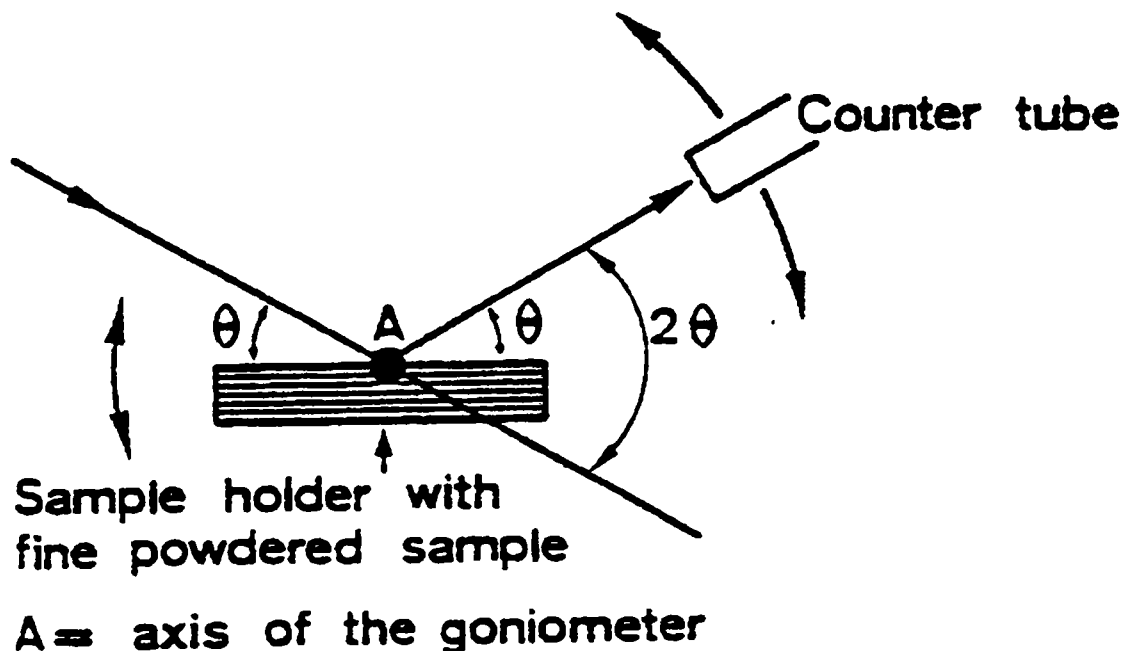
The diffraction method requires only small amounts (a few grams) of material.

The main application of X-radiation in the cement industry is that of X-ray fluorescence which is used for the determination of the chemical Composition of materials (see section 15, quality assurance, p. 15/33ff). The differences in principle (figure 38) and application between fluorescence and diffraction are briefly summarised in Table 31a.

Table 31a   Difference between x-ray diffraction and x-ray fluorescence

	Diffraction (XRD)	Fluorescence (XRF)
Application	Analysis of mineralogical composition	Analysis of chemical composition
Principles - Bragg-equation $2d \sin \theta = n\lambda$	determination of d-values according to 2θ ("fingerprint" of mineral) 2d : variable sin θ : variable λ : constant	determination of λ according to 2θ 2d : constant sin θ : variable λ : variable
- radiation (λ)	primary and diffracted radiation monochromatic with the same λ	primary radiation polychromatic, emitted radiation consisting of distinct characteristic wavelengths
- crystal structure (d-value)	identification of mineral according to d-value	special single crystal with defined d-value and orientation (analyzing crystal is used to disperse distinct characteristic wavelengths)

Fig. 37   **X-ray diffraction diagram**
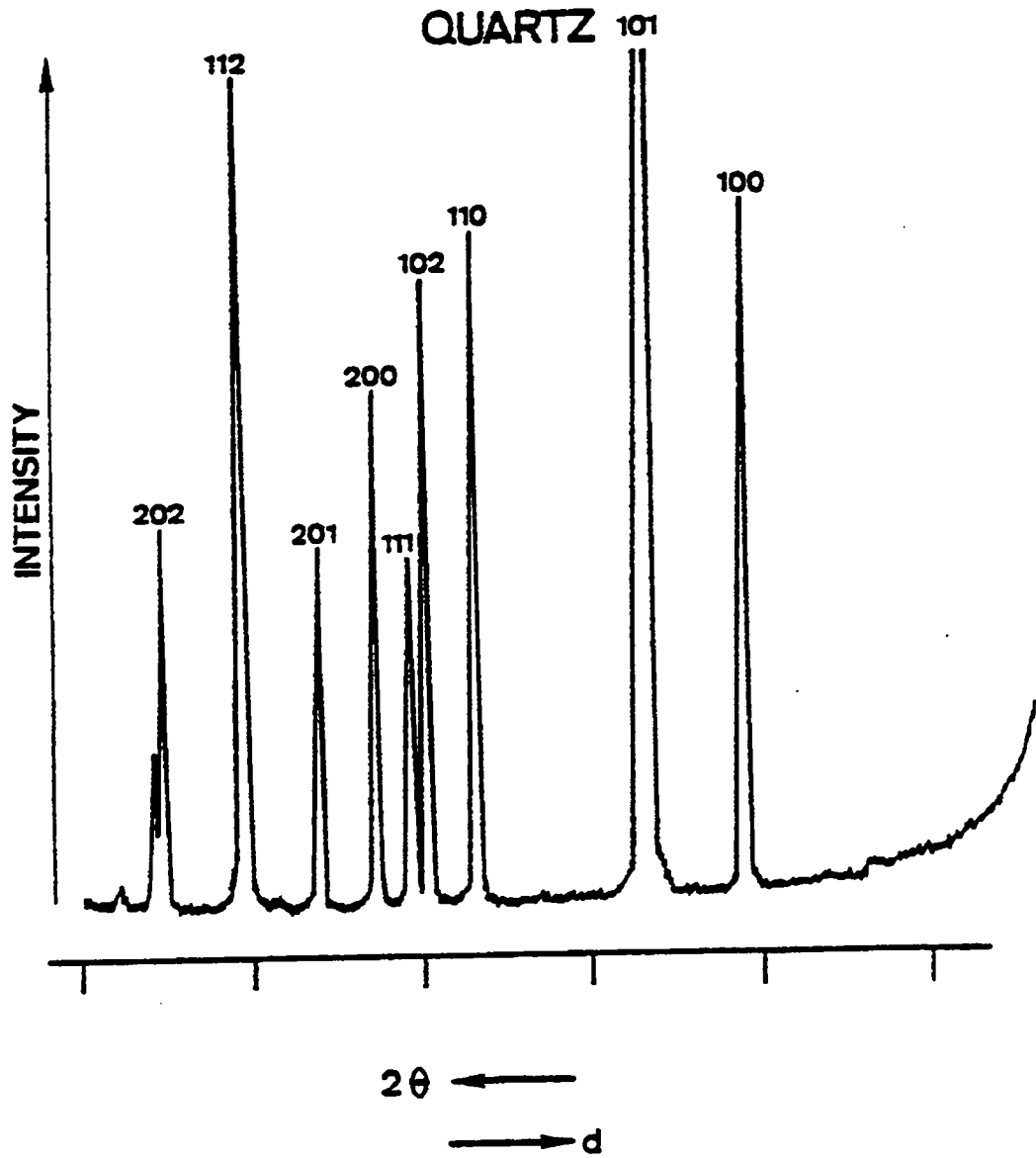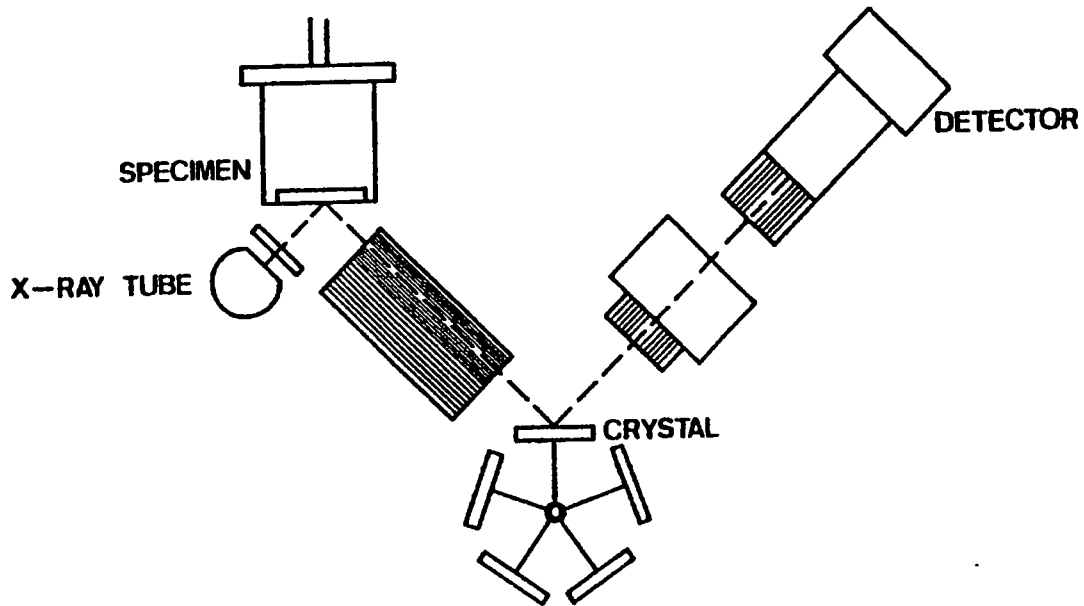
### Fig. 38   X-ray fluorescence spectrography

1.3.2.7 Polymorphism

An element or compound is defined as polymorphic if it forms two or more crystalline solid phases differing in atomic Arrangement with identical chemical Composition The polymorphism depends on pressure and temperature, i.e. a particular modification is only stable under defined pressure and temperature conditions.

As a consequence of polymorphism it occurs that materials with identical chemical Composition may exhibit different physical and chemical properties. A good example is pure carbon in graphite and diamond form. In the graphite form the carbon is black, soft, and is used, for example, as a lubricant or for electrodes. In the diamond form it is clear, transparent and hard a much coveted precious stone. The lattice structures of these two polymorphic crystalline forms are shown in Fig. 39.

Fig. 39   Lattice Structures of Carbon

$\beta - C$ $\alpha - C$

DIAMOND   GRAPHITE
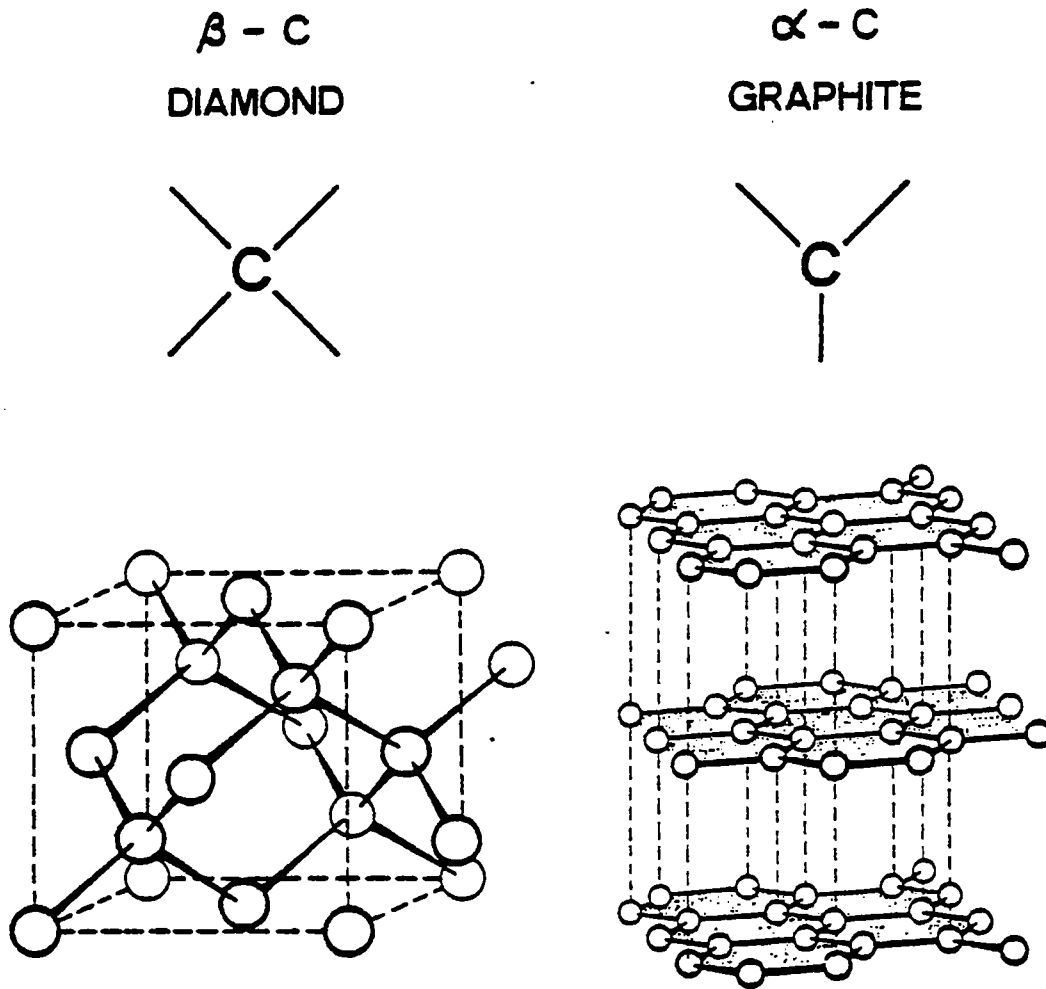
Further examples of polymorphism are:

♦ $CaCO_3$ as aragonite and calcite

♦ The crystalline forms of silica (SiO_2; see also p. 4/36.ff). At atmospheric pressure silica exists according to the temperature range in three crystalline forms (see fig. 40). Furthermore, each of the three forms exists in a low- and high-temperature modification (fig. 41 for quartz).
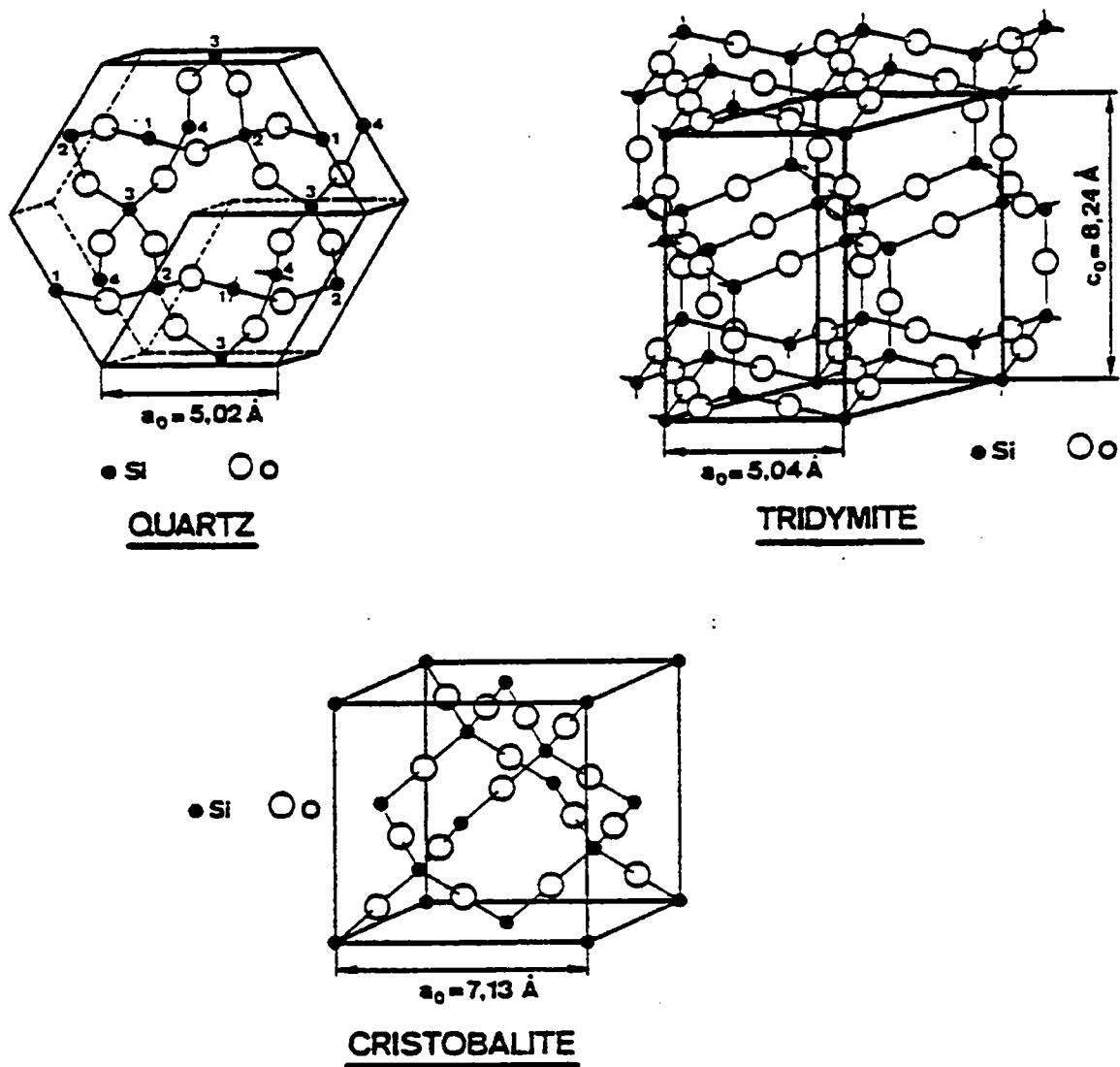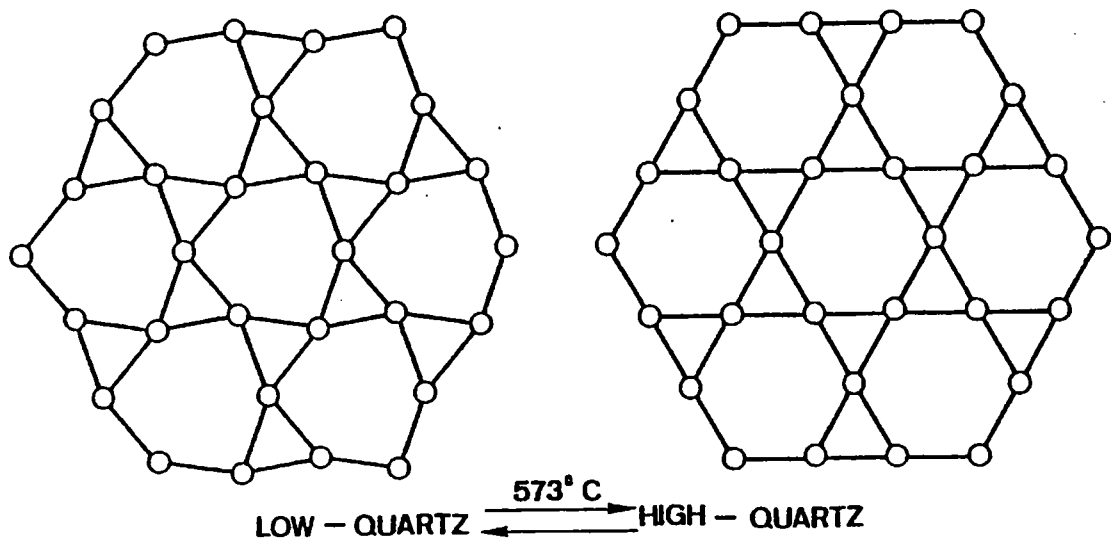
Fig. 40   Polymorphism of SiO$_2$

$a_0 = 5,02 \text{ Å}$

● Si   ○ o

QUARTZ

$c_0 = 8,24 \text{ Å}$

$a_0 = 5,04 \text{ Å}$

● Si   ○ o

TRIDYMITE

● Si   ○ o

$a_0 = 7,13 \text{ Å}$

CRISTOBALITE

Fig. 41   Si-Atoms in Low and High Quartz

$$\text{LOW} - \text{QUARTZ} \xleftarrow{573° C} \text{HIGH} - \text{QUARTZ}$$

1.3.2.8 Temperature Influence

The lattice points joined with lines producing a lattice are illustrated in Fig. 33. In reality, the atoms, ions and molecules are tightly packed in the crystal lattice with distances close to their atomic radii. The lattice forces, holding together the geometrical Arrangement of atoms, ions and molecules are of a physical and chemical nature.

At absolute zero temperature($0°K = -273°C$), the atoms are at rest with their centres in the equilibrium position. By raising the temperature, the atoms begin to oscillate: the higher the temperature, the stronger are their oscillations. With increasing temperature, the oscillation becomes so strong that the lattices may change their symmetry. This occurs at a defined, characteristic temperature. At even higher temperature, the atoms oscillate so violently that they leave the lattice places; the lattice literally falls apart; the crystal melts.

Conversion of the raw material into clinker in a cement kiln requires a high temperature which means high energy. This is the energy required to destroy the crystal lattices of the raw material minerals in order to transform them into crystal lattices of clinker minerals. The energy necessary to destroy the lattice depends an the lattice forces, i.e. on the crystal system, the lattice constants, the nature of atoms and ions, and on the perfection of the lattice. This explains why one particular raw material is more easily burned to clinker than another. Therefore, the type and state of the crystals present in the raw material determine burnability, i.e. the energy required to form the clinker.

Minerals with strong lattice forces which impair the burnability are : quartz and feldspars
Minerals with weaker lattice forces and thus better burnability are : clay minerals
Materials with a highly disordered structure, showing high reactivity are : amorphous and glassy rocks such as tuff, lava, amorphous silica, etc.

1.3.3 Mineralogical Characteristics

1.3.3.1 General

Mineralogy is concerned with crystalline solids all kinds, whether natural or industrial. Crystalline solids of all kinks, whether natural or industrial. Crystalline solids come in endless variety: the rocks of the earth's crust, the concrete of buildings and steel are a few examples of materials composed of crystals.

1.3.3.2 Minerals and their Properties

For the sake of practicality, minerals are classified into rock-forming minerals, ore minerals, clinker minerals, slag minerals, natural gemstones, synthetic gemstones, ceramic phases, etc. Whether these are natural or artificial is irrelevant; all are crystalline phases.

The properties of minerals depend upon the crystal structure (type of crystal lattice), lattice forces (arrangement and chemical binding of atoms) and lattice energy.

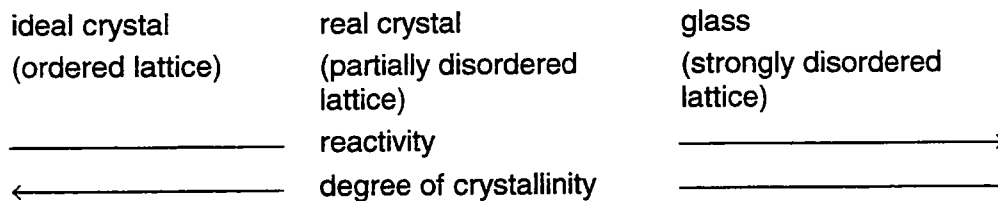Apart from the chemical composition (4.3.1)the most important properties with regard to the cement-making process are:

♦ Reactivity and kinetic behaviour

In many cement raw mixes, the minerals are in a stable condition with low free energy, and therefore, a low reactivity. To produce clinker minerals much energy is needed to destroy the structure of the raw materials and to form new structures (clinker minerals).

The following phenomena improve the reactivity of minerals:

• impurities (atoms, ions, molecules) disturbing the ideal crystal lattice

• lattice defects

They give the crystal structure a higher degree of disorder which is equal to a lower degree of crystallinity:

ideal crystal (ordered lattice)	real crystal (partially disordered lattice)	glass (strongly disordered lattice)
	reactivity —————————————→	
←————————————— degree of crystallinity		

At room temperature conditions, a mineral or a mineral combination of raw mix is in a stable condition To let a reaction take place, at least one condition pressure or temperature - has to be changed. The crystal lattices of the minerals present in the raw mix have to be disintegrated in the course of the clinkering process. This is best achieved by applying a high temperature. The minerals thus become unstable. As there is always a tendency from unstable towards stable conditions, reactions leading to a new equilibrium take place.

The equilibrium can be attained by e.g.:

♦ modification changes of minerals

♦ melting and evaporating reactions

♦ chemical reactions between the different minerals with the formation of new minerals

While the correct chemical raw mix composition is a requirement for the clinker phases, the mineralogical characteristics of the mix determine how the reactions leading to these clinker phases take place. Because of the broad variability of mineralogical properties, many different paths of reaction exist (more details are given in section 10 concerning clinker manufacture).

Hardness

Hardness is defined as the resistance of a mineral to scratching. A scale of relative hardness was introduced by Mohs. The Mohs scale contains 10 hardness classes each characterised by specially selected minerals (refer Table 34, p.55 and Table 35, p.56

Other mineral properties are:

- Density
- Cleavage and fracture
- Electrical properties
- Heat conductivity and heat expansion
- Surface properties

1.3.3.3 Determination of Minerals

For identification and quantification of minerals, the chemical analysis is usually combined with:

- x-ray diffraction analysis
- thermal analysis
- light microscopy

1.3.3.4 Minerals in Cement Raw Materials

Basically, a preliminary grouping of the minerals is accomplished by the chemical Composition whereby the mineral formulae sometimes have to be idealised.

Carbonates

Calcite	$CaCO_3$ trigonal	) polymorphic
Aragonite	$CaCO_3$ orthorombic	)

Aragonite and calcite are polymorphic modifications with an identical chemical Composition but with different crystal lattices. Aragonite is formed in the warm and shallow sea. It is unstable and transforms readily to calcite and can thus be found only in recently deposited unconsolidated sediments.

Other carbonates are:

| Magnesite	$MgCO_3$
Siderite	$FeCO_3$
Dolomite	$CaMg(CO_3)_2$
Ankerite	$Ca(Mg, Fe)(CO_3)_2$

Calcium sometimes may be substituted by significant amounts of other elements such as Mg, Mn and Fe; for example: Mg-bearing calcite $Ca_{1-x}Mg_xCO_3$ (not identical with dolomite).

Carbonates have an excellent cleavage and a Mohs-hardness of 3 - 4.

Silicates

The lattice of all silicates are based on the SiO_4-tetrahedron (Fig. 42). One Si-atom is situated in the centre of the tetrahedron, whereas the four corners are occupied by oxygen atoms.

Fig. 42   Structure unit of Silicates: SiO_4-Tetrahedron.
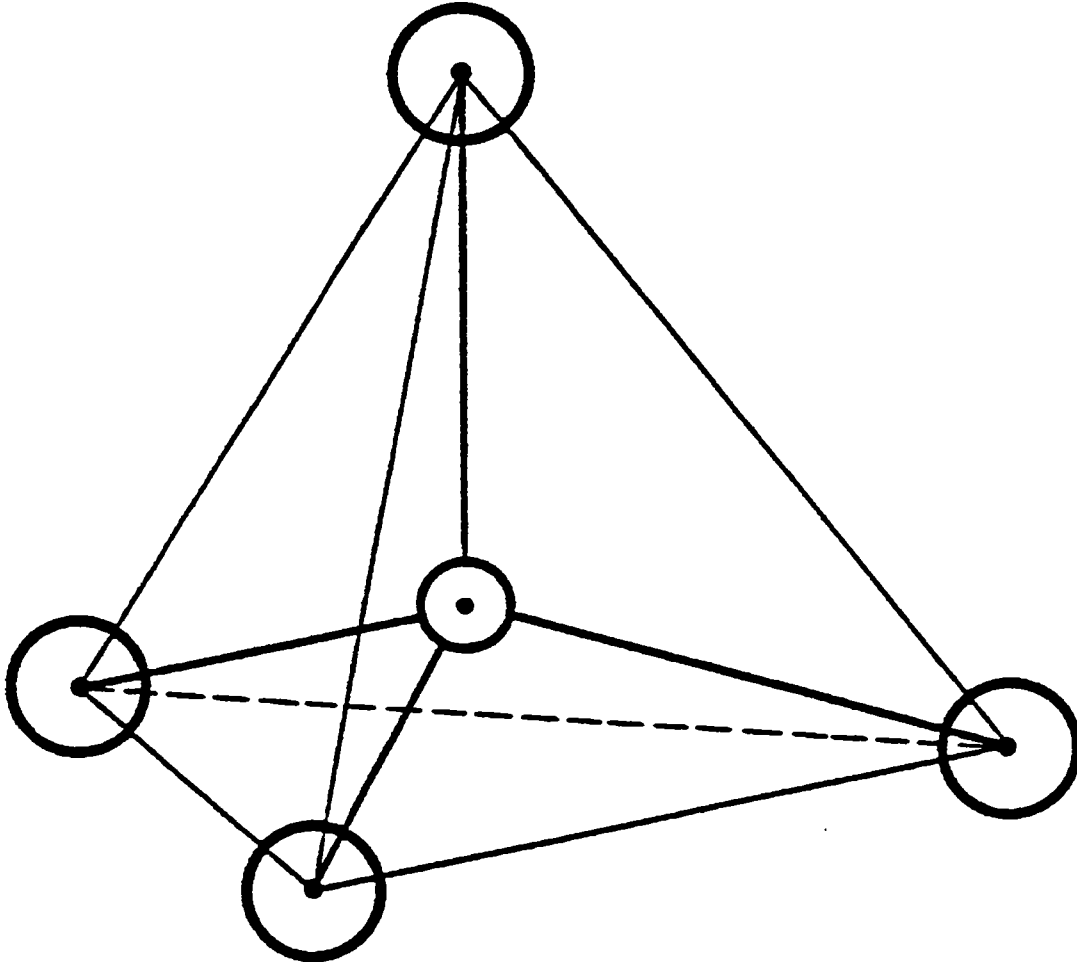
SiO_4-tetrahedra can be combined in different ways (Fig. 43 - 46) leading to different silicate types:

single tetrahedron	- nesosilicates :	olivine and garnet groups
double tetrahedra	- sorosilicates. :	epidote group
rings	- cyclosilicates :	tourmaline, beryll
single and double chains	- inosilicates	pyroxene and amphibole groups
sheets	- phyllosilicates:	mica and clay mineral groups
framework	- tectosilicates:	feldspar group

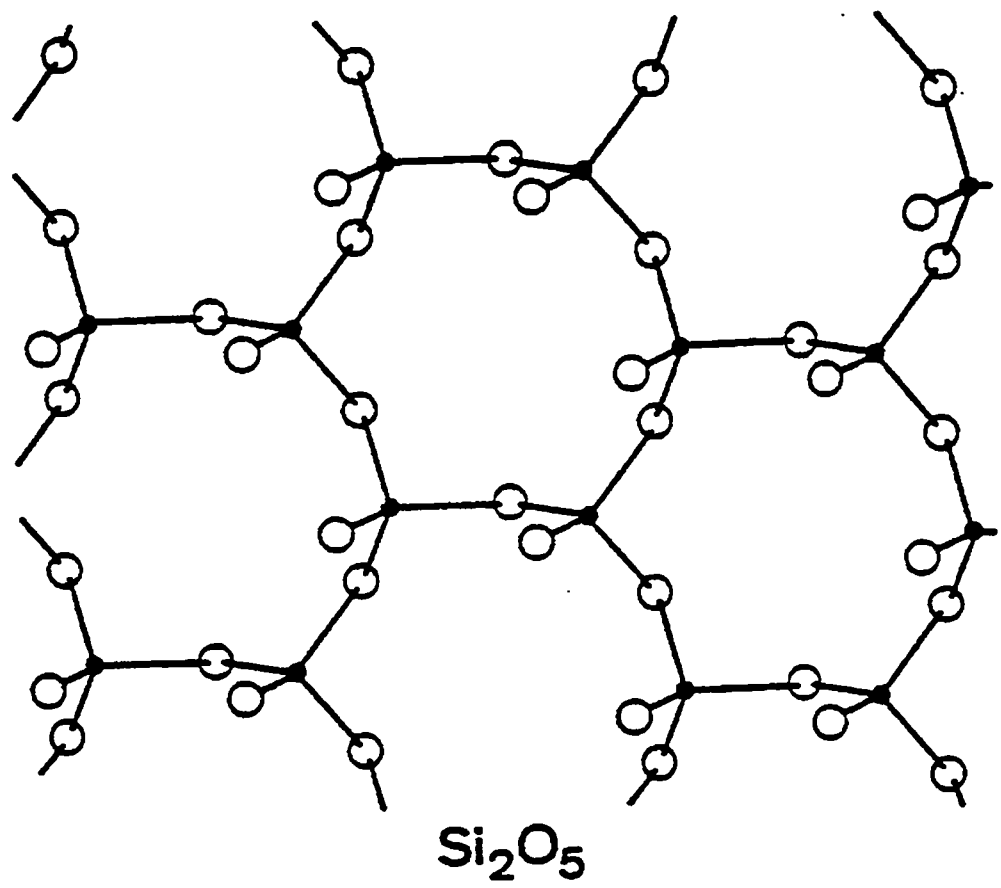**Fig. 43**   **Types of linkage of SiO₄-Tetrahedra (single/double/rings).**
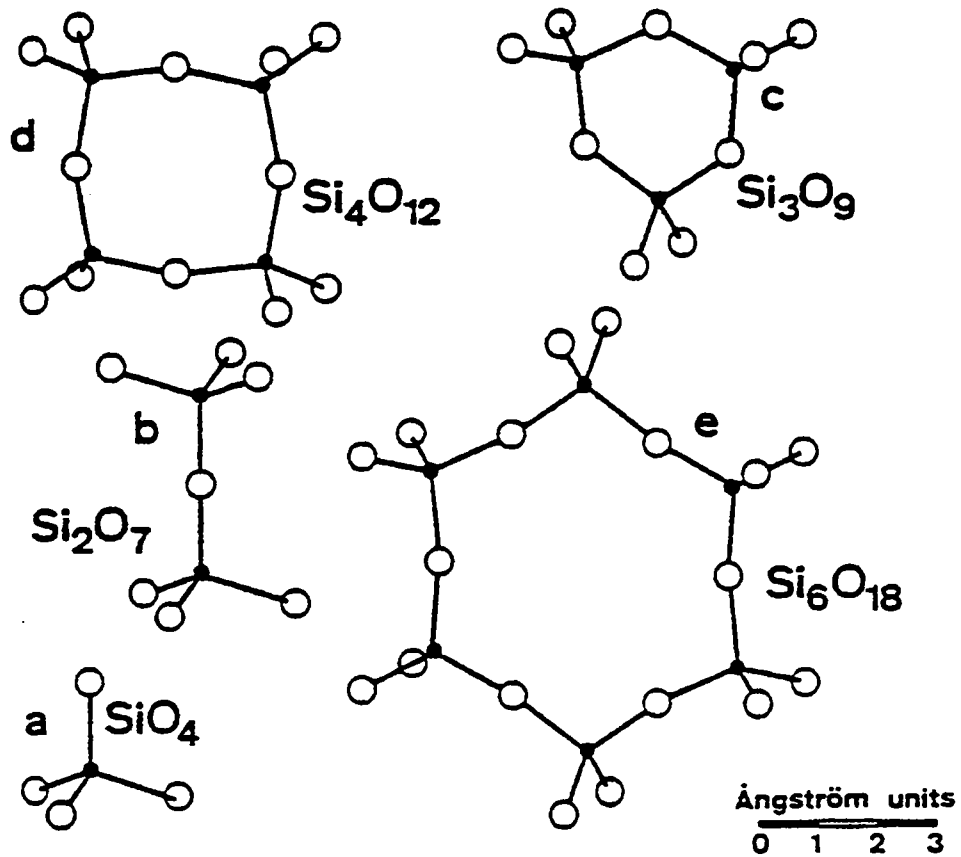
a)   SINGLE TETRAHEDRON

b)   DOUBLE TETRAHEDRA

c) ⎫
d) ⎬ RING STRUCTURES
e) ⎭

Fig. 44   **Types of linkage of SiO_4-Tetrahedra (chains - single/double).**
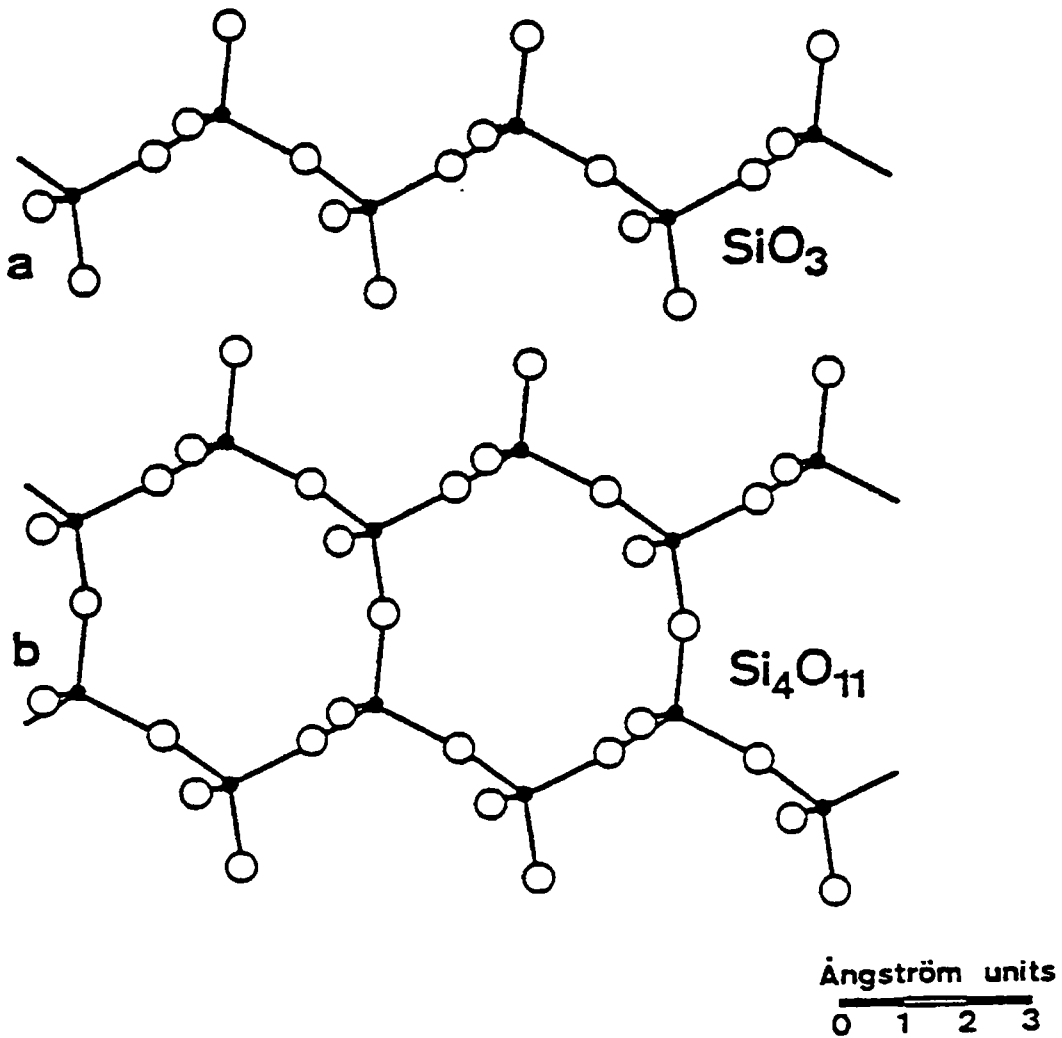
a) SINGLE CHAIN STRUCTURE

b) DOUBLE CHAIN STRUCTURE

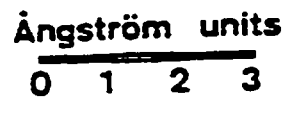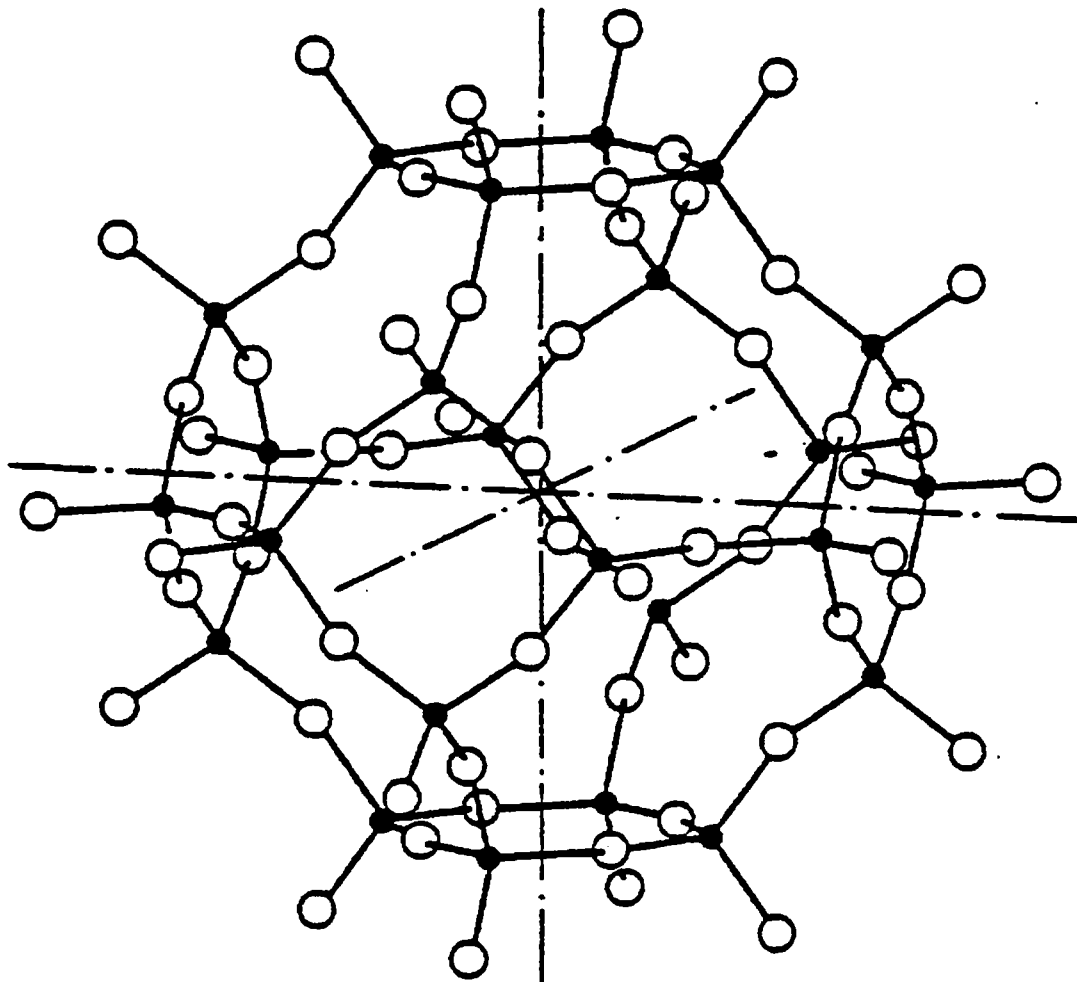**Fig. 45**   **Types of linkage of SiO$_4$-Tetrahedra (Sheets).**

$$Si_2O_5$$

SHEET STRUCTURE

Ångström units

0   1   2   3

Fig. 46   **Types of linkage of SiO$_4$-Tetrahedra (Framework).**

$$SiO_2$$

THREE DIMENSIONAL FRAMEWORK

Ångström units

0   1   2   3

The fact that so many possibilities to combine the structural unit exist, may explain why the silicate group contains a large number of different minerals (about 500). The Si of the SiO$_4$-tetrahedron may be replaced by Al; and nearly all silicate structures show the ability of exchanging cations (Na, K, Ca, Mg, Fe, Al, etc.). Within the structure of many of the resulting lattices, there is free space left for different cations (e.g. Na, K, Ca, Al, Mg).

The amount of silicates in the earth's crust is estimated to be about 90 %.

As indicated on page 4/36, the group of silicates consists of several structural types such as:

Feldspar Group

Feldspars are the most abundant of all minerals. They occur in almost all siliceous components used in cement raw mixes. By alteration and weathering feldspars change into clay minerals.

Most abundant feldspars are:

Alkali feldspar series $(K, Na) AlSi_3O_8$	orthoclase	$KAlSi_3O_8$
	Albite	$NaAlSi_3O_8$
Plagioclase series $(Na, Ca)(Si, Al)AlSi_2O_8$	Anorthite	$CaAl_2Si_2O_8$

All feldspars show good cleavage and a Mohs-hardness of 6.

Clay Minerals and Micas

Clay minerals usually are the most important siliceous compounds of cement raw mixes. Crystal lattices of clay minerals can be characterised as shown in Figs. 47 to 49.

Fig. 47   Clay Mineral Structures (two-layer structures).

SERPENTINE   KAOLINITE   HALLOYSITE

⊙ Mg   ○ Al   •Si   ○H$_2$O   ○O,OH

Å
0   2   4   6   8   10
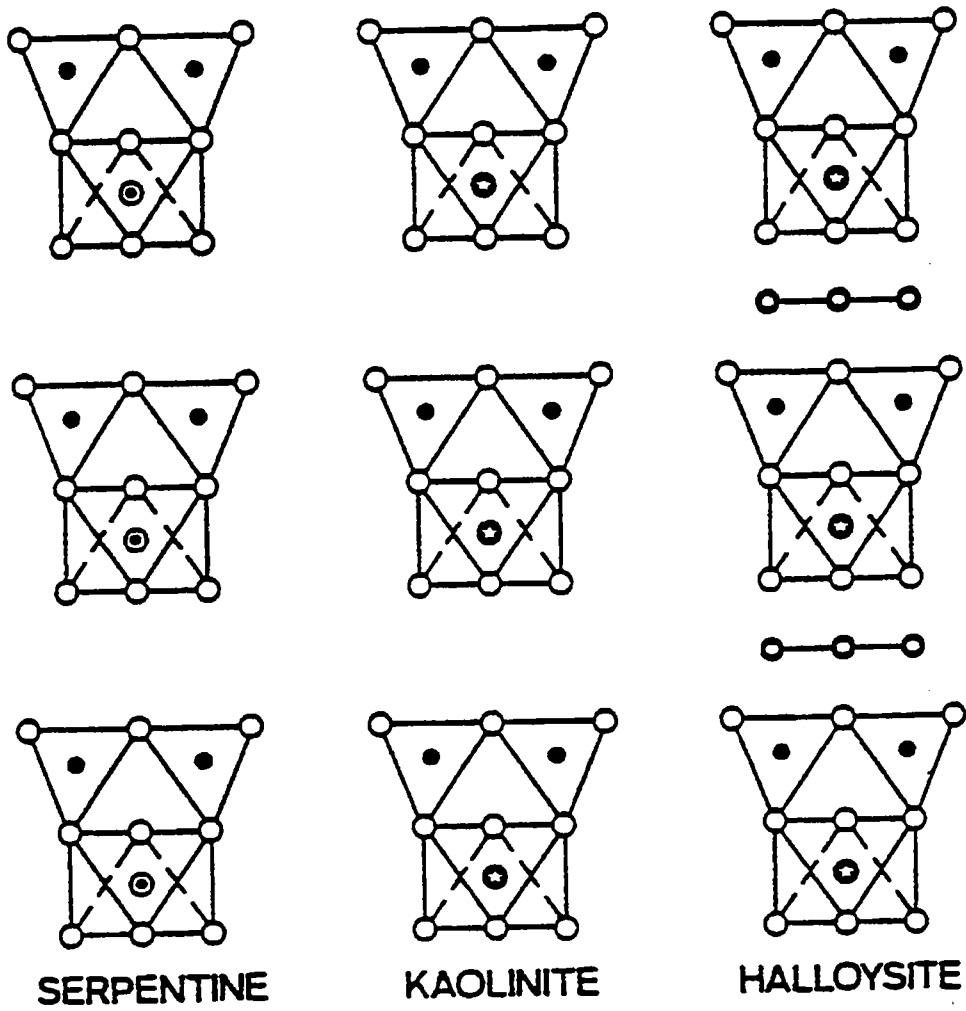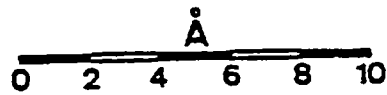
Fig. 48   Clay Mineral Structures (three-layer structures).

THREE-LAYER STRUCTURES
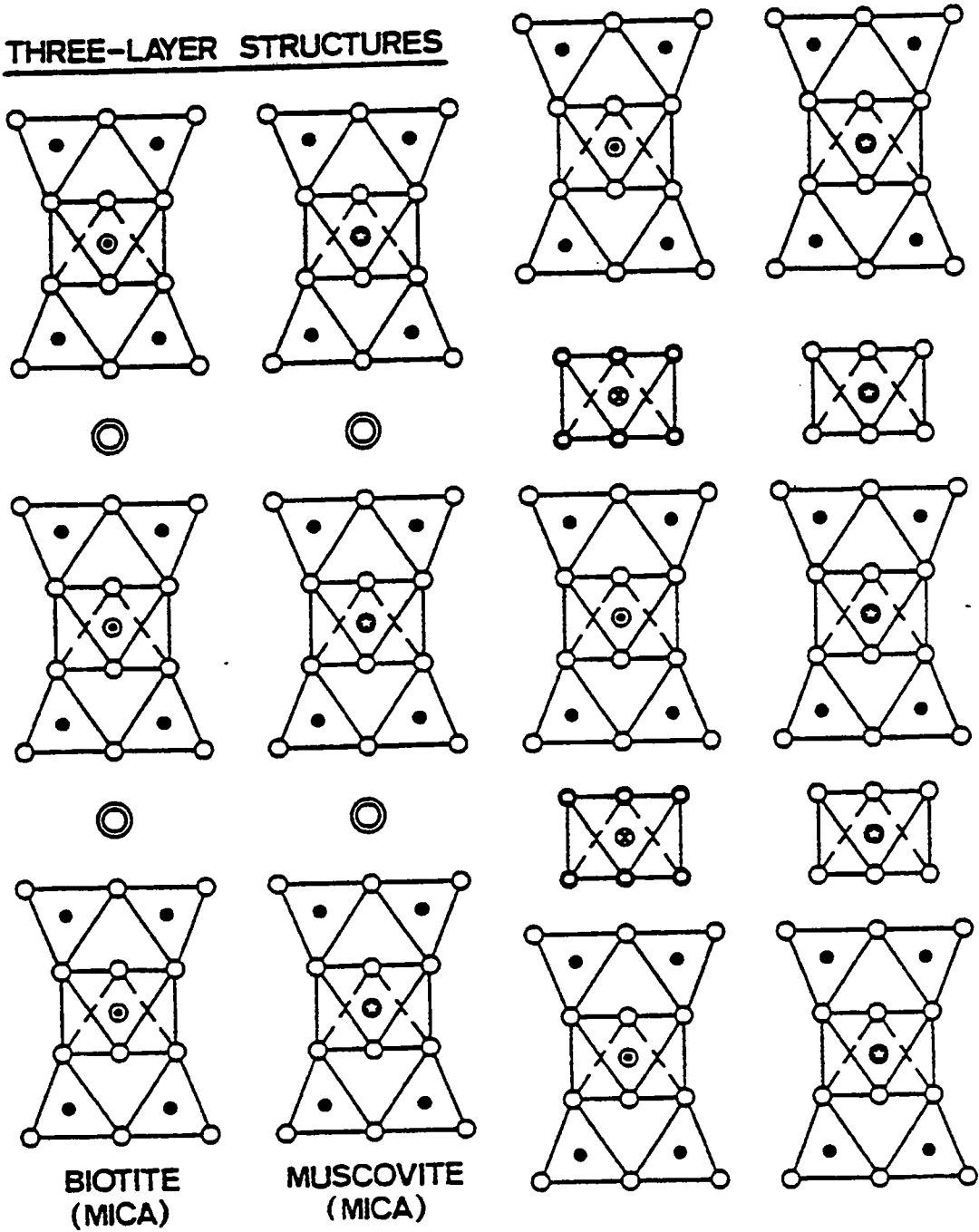
BIOTITE
(MICA)

MUSCOVITE
(MICA)

MONTMORILLONITE
VERMICULITE

CHLORITE

⊚ Mg   ○ Al   ● Si   Ⓚ K   ○ H₂O
⊕ EXCHANGEABLE CATIONS
○ O, OH

Å
0   2,5   5

Fig. 49   Clay Mineral Structures (two and three-layer structures).

$\beta = 105°$

715 Å

c axis

b axis

6 (OH)

4 Al

2 (OH) + 4 O

4 Si

6 O

TWO-LAYER STRUCTURE (KAOLINITE)

14,3 Å

c axis

b axis

6 O

3 Si + 1Al

2 (OH) + 4 O

5 Mg + 1Al

2 (OH) + 4 O

3 Si + 1Al

6 O

THREE-LAYER STRUCTURE (CHLORITE)
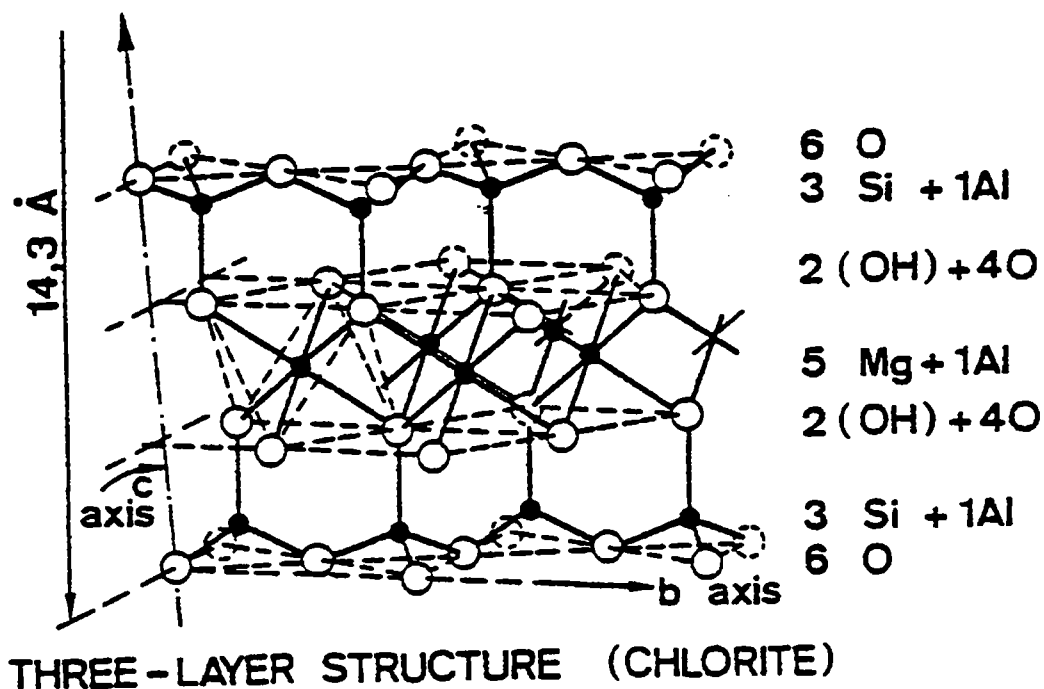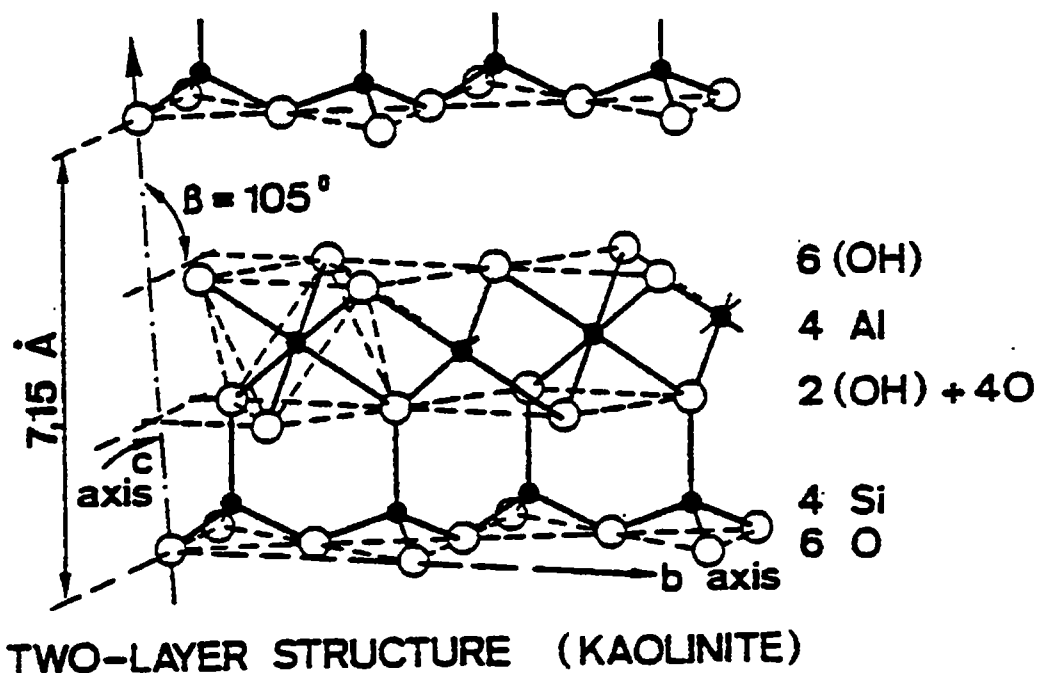
The main structure unit is again the SiO_4-tetrahedron. In addition, a new unit having the shape of an octahedron appears. The centre of the octahedron is occupied by a cation (e.g. Al, Mg), the corners by O or OH-Groups (structurally bound water). The structure of a clay mineral may contain layers of Tetrahedra and octahedra and combinations of both structural elements. The dimensions of the tetrahedral and the octahedra layers are very similar. Composite tetrahedral-octahedral layers are readily formed leading to a two-layer structure. Similarly, an octahedral layer sandwiched between two tetrahedral layers forms a three-layer structure. Between these two-layer or three-layer packages different cations and/or H_2O-molecules can be situated.

The many possibilities of combining the structural units are responsible for the existence of numerous clay minerals.

The macro and microscopic appearance of clay minerals corresponds to the internal layer structure (phyllosilicates). Properties which are very typical for clay minerals are explained by the characteristics of their crystal lattice.

Relevant features of clay minerals are:

◆ Water adsorption capability : the water is absorbed in three different ways:

  ● in pores between single crystals and crystal Aggregates

  ● directly on the surface as "adsorptive water" due to the dipole character of the H_2O-molecule; this water particularly causes clay mineral properties such as plasticity and thixotropy.

  ● as "interlayer water" between the two- or three-layer packages in the crystal lattice, causing expansion of clay minerals.

◆ Capability of ion exchange : the ions placed between the layers of the crystal lattice e.g. Na^{+} K^{+}, NE^{+}, SO_4^{-}, Cl^{-}, are easily exchangeable.

◆ Thermal behaviour : of special interest are the temperatures of loss of water. Generally, pore water, adsorbed water and interlayer water are set free at temperatures between 100 ° and 300 +C. The structurally bound water (OH-groups) is driven off in the range of 400º - 900ºC. Depending on the type of clay mine -1, the loss of the 'water types" mentioned above occurs at defined temperatures or continuously in a certain temperature range.

Important clay minerals and micas (see also Fig. 47 to 49) are:

Kaolinite group:

Kaolinite $Al_2Si_2O_5 (OH)_4$
Halloysite $Al_2Si_2O_5 (H_2O)_4$
low plasticity, without inlayer cations

Palygorskite:

$Mg_{2.5} (H_2O)_2(CH)Si_4O_{10} . 2 H_2O$
properties partially similar to montmorillonite and vermiculite with ability to take up and retain large quantities of water

Montmorillonite:

$Al_2Si_4O_{10} (OH)_2 - x H_2O$
varieties with Na, K, Fe, Mg, etc., especially capable of exchanging ions, large content of interlayer water possible, optimum plasticity therefore with water contents from 80 % up to 250 %, thixotropic behaviour of clay suspensions or slurries, capability of expansion

Vermiculite:
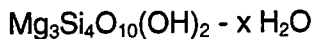
$Mg_3Si_4O_{10}(OH)_2$ - x H_2O
properties partially similar to those of montmorillonite, shows rapid and large expansion on heating.

Illite (Hydromica):

$(K, H_2O)Al_2AlSi_3O_{10}$ $(H_2O, OH)_2$ usually poorly crystallised, plasticity can be high depending on degree of crystallinity.

Micas:

- Biotite
  $K(Mg, Fe)_3 AlSi_3O_{10} (OH)_2$

- Muscovite
  $KAl_2AlSi_3O_{10} (OH)_2$ usually well crystallised, no plasticity.
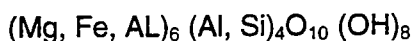
Chlorite series:

$(Mg, Fe, AL)_6 (Al, Si)_4O_{10} (OH)_8$

Mixed Layers are more or less regular combination of lattices of different clay minerals, e.g. of illite-montmorillonite by combination of two- and three-layer structures. The properties are usually close to those of montmorillonite.

Silica

SiO_2 occurs in several polymorphic forms (see 4.3.2.7) each of them being stable in different temperature ranges under atmospheric pressure:

Low-Quartz	< 573°	triconal
High-Quartz	573° - 870°c	hexagonal
Tridymite	870° - 147° c	hexagonal
Cristobalite	1470°- 1715°c	isometric
Liquid	>1715° c	

Amongst the crystalline forms of SiO_2, low-quartz is the most abundant modification with a Mohs-hardness of 7, without cleavage and with conchoidal fracture. With the transformation of quartz to tridymite and cristobalite, an increase in volume occurs. SiO_2 also exists in a more or less amorphous modification, which has been formed by gradual dehydration of water containing silica-gel. This modification is known as:

Opal or Silex: SiO_2 . x H_2O with Mohs-hardness of 5½ - 6½

SiO_2 also occurs in almost sub-microscopic and fibrous varieties which are known as:

- Chalcedony
- Agate
- Jasper
- Chert
- Flintstone

Because of their fibrous structure, these varieties are very hard and tough.

Hydroxides

Hydroxides are formed at the earth's surface by weathering action under humid climatic conditions. They occur in many sedimentary rocks. Common hydroxides are:

- Gibbsite (Hydrargillite) $Al(OH)_3$
- Diaspore, Boehmite $AlOOH$
- Goethite, Lepidocrocite $FeOOH$
- Limonite $FeOOH - n\ H_2O$

These minerals usually have a low degree of crystallinity and are quite reactive.

Oxides

Some of the minerals of this group are present as minor components in many rocks. They predominate in certain ores which sometimes are used as correctives in cement raw mixes.

Abundant oxides are:

- Magnetite Fe_3O_4
- Haematite Fe_2O_3
- Ilmenite $FeTiO_3$

Sulphides

The most abundant sulphide is:

- Pyrite FeS_2

which is frequently employed as Fe-corrective after roasting to oxide (pyrite ash or pyrite cinders).

Sulphates

Two naturally occurring sulphates are important:

- Gypsum $CaSO_4 . 2\ H_2O$
- Anhydrite $CaSO_4$

They are added to the clinker to produce cement.

1.3.4   Rock Characteristics

1.3.4.1 Definition

Rocks are combinations of one or more kinds of minerals being stable under given conditions of pressure and temperature.

Equilibrium conditions exist between the minerals of a rock as well with respect to the surrounding of the rock (conditions of low free energy). If the conditions change for some reason, reactions towards a new equilibrium occur. This is possible in the system itself by reactions between minerals present in the rock or by reactions with agents introduced to the system from outside.

In nature, reactions of this kind are involved in rock metamorphosis and weathering. Metamorphosis can be schematised as follows:

Pressure	P_1	H_2O	Pressure	P_2
Temperature	T_1	CO_2 $\uparrow$	Temperature	T_2
Rock	A	$\Rightarrow$	Rock	B
Minerals	a, b, c		Minerals	a, b, e, f
Chemical Composition I			Chemical Composition II	

In the case of rock weathering, agents from outside are added to the system (water, air);

Pressure	P_1	H_2O	Pressure	P_3
Temperature	T_1	O_2 $\downarrow$	Temperature	T_3
Rock	A	$\Rightarrow$	Rock	C
Minerals	a, b, c		Minerals	a, b, e, f
Chemical Composition I			Chemical Composition II	

The process of clinker formation can be compared, to some extent, with rock metamorphosis.

1.3.4.2 Properties of Rocks

The more important rock characteristics to be considered in the course of cement production are:

♦ chemical composition

♦ type and condition of minerals building up the rock

♦ grain size, distribution and geometrical Arrangement of the minerals (or of the rock fragments) which can appear as rock compounds

♦ as well. These features are summarised by the expression "rack texture'.

♦ cleavage

♦ degree of consolidation

1.3.5 Physical Characteristics; Engineering Properties of Rocks

The physical properties of rocks are as important as the chemical and mineralogical characteristics because they are determining factors in the choice of method and technique of raw material exploitation, transportation, blending and comminution. They therefore affect the manufacturing process.

1.3.5.1 Density and Porosity

The term "specific weight" or density is used for the weight of a unit of volume of a specimen, dried at 105°C, excluding all pores.

The term "specific gravity" includes the-volume of the pores per unit of volume of a specimen (Table 32).

"Bulk density" refers to comminuted material, i.e. means weight per unit of volume.

"Porosity" or "pore volume" expresses the hollow space of pores and voids in percent.
Porosity (Table 32) as:

volume of pores
total volume

With regard to the sedimentary rocks, porosity depends largely on the amount of cementing material present and the size, grading and packing of the granular constituents.

Other physical properties (e.g. strength) also depend on the porosity.

Table 32 Density and porosity of rocks

Rock	Specific gravity (density) g/cm	Porosity %
Granite	2.5 -2.8	0.5 - 1.5
Diorite	2.6 -2.9	0.1 - 0.5
Gabbro	3.0 -3.1	0.1 - 0.2
Dolerite	3.0 -3.1	0.1 - 0.5
Rhyolite	2.4 -2.6	4 - 6
Andesite	2.2 -2.3	10 - 15
Basalt	2.8 -2.9	0.1 - 0.2
Tuff	2.8 -3.0	high
Sand (loose)	1.5 -2.0	25 - 50
Sandstone (compacted)	2.0 -2.6	10 - 30
Shale	2.0 -2.4	10 - 30
Limestone	2.2 -2.6	5 - 20
Dolomite	2.5 -2.6	1 - 5
Marl	1.6 -2.6	5 - 30
Clay	1.5 -1.9	30 - 50
Claystone	1.8 -2.3	15 - 35
Gneiss	2.9 -3.0	0.5 - 1.5
Marble	2.6 -2.7	0.5 - 2
Quartzite	2.6 -2.7	0.1 - 0.5
Slate	2.6 -2.7	0.1 - 0.5

1.3.5.2 Water Absorption

Phenomena, such as consistency, plasticity, swelling, etc. are functions of porosity or water absorption. Loose material absorbs considerably higher quantities of water than compact material. The water absorption capability is increased significantly in the presence of clay minerals. Three kinds of absorption are distinguished: pore water, water accumulation on clay mineral surfaces ("adsorption water"), and water penetrating the clay mineral structure ("structural water"). The latter kind may lead to swelling. Water absorption of clay minerals increases

from	illite	high crystallinity
	Kaolinite	high crystallinity
⇓	Kaolinite	low crystallinity
	illite	low crystallinity
to	Montmorillonite	

1.3.5.3 Rock Strength

Compressive strength increases with:

♦ increasing content of minerals with high compressive strength potentials

♦ increasing content of cementing matter (increasing degree of intergrowth of minerals)

♦ decreasing grain size

and decreases with:

♦ increasing amount of minerals with good cleavage

♦ increasing porosity

♦ increasing content of micro-joints

♦ increasing degree of weathering

♦ increasing moisture absorption capability

Table 33: shows same compressive strength for different rocks.

Table 33   Compressive strength of rocks

Rock type	Compressive strength kg/cm^2 / N/mm^2	Valuation (of compressive strength)
Basalt Quartzite	> 2800 / > 280	very high
Granite Diorite Limestone	1800 - 2800 / 180 - 280	high
Sandstone Limestone Marble Slate	800 - 1800 / 80 - 180	medium
Porous Limestone	400 - 800 / 40 - 80	low
Chalk, Tuff, Shale, Clay, Claystone	< 400 - < 40	very low

1.3.5.4 Rock Hardness

There is no absolute Definition of the term "rock hardness". Today, the terms "hard rock" or "soft rock" are occasionally used in practical fieldwork. Rock hardness is not only determined by the mineral content but also by the degree of intergrowth of the individual minerals. It is commonly expressed by the compressive strength.

The mineral hardness can be measured by means of the scratch method according to Mohs (Tables 34 and 35).

Table 34   Hardness of most abundant minerals according to Mohs

Mineral	Mohs scale	Valuation
Quartz	7	
Feldspar	6	"hard"
Pyroxene	6	minerals
Amphibole	6	
Calcite	3	
Dolomite	3.5	"soft"
Mica	3	minerals
Chlorite	2-3	
Clay minerals	2	

Table 35   Hardness Scale

Old MOHS scale	Hardness classes	Microhardness kg/mm²	Hardness classes	New MOHS scale
Diamond - 10				Industrial diamond (111)
	15	10000	15	Diamond - Carbonado
	14	9000 / 8000	14	
	13	7000	13	$B_{6.5}C$
		6000		
	12	5000	12	B_4C
	11	4500 / 4000	11	Boron
	10	3500 / 3000	10	TiC
Corundum - 9	9	2500	9	Corundum (11$\bar{2}$0)
		2000		
Topaz - 8	8	1500	8	Topaz (001)
Quartz - 7	7		7	Quartz (10$\bar{1}$1)
Orthoclase - 6		1000 / 900 / 800 / 700 / 600		
Apatite - 5	6		6	Magnetite (111)
	5	500 / 400	5	Scheelite (111)
		300		
Fluorite - 4	4	200	4	Fluorite (111)
Calcite - 3				
Gypsum - 2	3	100	3	Galena (100)
	2	50	2	Halite (100)
Talc - 1	1	10 / 5	1	Talc (001)
		1		

1.4 PRINCIPLES OF RAW MATERIAL ASSESSMENT

1.4.1 Chemical Parameters

A check-list for the assessment of a Potential cement raw material is given in Table 36, comprising basic chemical features.

Table 36   Check-list for potential cement raw material (chemical)

Components	Parameters to be checked	Limits (guide lines)
Calcareous materials (limestone, etc.)	Carbonate titration as $CaCO_3$ MgO content SO_3 content P_2O_5 content Cl	> 80 % < 4 % < 1 % < 1 % < 0.1 % *
Argillaceous materials (clay-marl)	Total alkali as Na_2O equivalent (Na_2O + 0.66 K_2O) Al_2O_3 content SO_3 content CL content	depending on cement type > 10 % < 1 % < 0.1 %
Correctives for aluminium (bauxite, laterite) for iron ore (pyrites ash) for silicon (quartz sand) for calcium (high-grade limestone)	 Al_2O_3 content Fe_2O_3 content SO_3 content SiO_2 content $CaCO_3$ content MgO	> 25 % (Tab. 22) > 60% < 5 % >80 % > 90% < 2 %
Additives (tab. 23) (gypsum)	SO_3 content	> 35 %

* limit variable according to process

In addition, the mineralogical characteristics have to be checked (Table 37).

Table 37   Check-list for Potential cement raw materials (mineralogical)

Components	Parameters to be checked	Limits (guide lines)
Calcareous materials (limestone, etc.)	Calcite Aragonite Dolomite	> 80% < 5% < 5%
Argillaceous materials (clay, marl)	Clay minerals	> 30%

1.4.2   Deleterious Constituents in Cement Raw Materials

"Deleterious constituents" are defined as components which:

♦ adversely affect the quality or marketability of cement

♦ appreciably increase production costs through difficulties in exploitation, reparation and processing in the kiln

In fact, the limits established in Tables 36 and 37 are already referring to these constituents. The major deleterious constituents (if occurring in higher amounts) are K_2O and Na_2O, MgO, SO_3, P_2O_5, CL, etc. In addition to these oxides, there are other, less important, deleterious constituents including Cr_2O_3, Mn_2O_3, F, etc.

They are always present in small amounts and are usually not considered for the mix calculation. If the concentration of certain minor and trace elements becomes too high, components otherwise suitable for cement manufacturing have to be rejected or limited in amount. Suddenly occurring difficulties in a plant very often are caused by an increase of the content of some minor and trace elements in the raw mix. Most minor and trace elements can have a deleterious effect on the production process as well as on the cement quality. On the other hand, it is known that a small amount of such elements is necessary to stabilise certain modifications of clinker minerals which are preferred to be present in an industrial clinker. The maximum content of some of these elements having a well known deleterious influence on the cement quality is limited by the specifications (e.g. MgO).

The following description gives a summarised survey of the most important minor elements and of the influence they have:

Alkalis

The term 'alkalis" as used in the cement industry" refers to the oxides of potassium (K_2O) and sodium (Na_2O). Alkalis occur mainly in minerals (Tables 38, 39) which are components of igneous rocks or their weathered products, such as clay and sandstone.

Table 38   Alkali sources in cement raw Materials

Rock type	minerals	Deleterious	constituents
<u>Igneous rocks</u> Granite Rhyolite Diorite Lava Tuff	Feldspars: Albite orthoclase Andesite Micas: Muscovite Biotite	 11.8 % 16.9 % 5.9 -8.3 % 1.8 % 10 -11 %	 Na_2O K_2O Na_2O K_2O K_2O
<u>Sediments</u> Clay Shale Sandstone (marl)	 Feldspars Micas Illite	 as above 10 - 11.8 % 5.5 %	 K_2O K_2O

Alkalis may cause problems particularly in the kiln section, since they are volatilized quite easily. Together with other volatile constituents, such as chlorine and sulphur, they may cause build-ups in the form of rings, cloggings, etc. in kilns and preheaters. Furthermore, an alkali content of > 0.6% (total alkali as Na_2O equivalent) may react with the amorphous silica present in some concrete aggregates producing alkali silica gels which have a great affinity for water. The resulting osmotic pressures may cause disruption of concrete. On the other hand, the initial strength development of concrete.

MgO

MgO is predominantly supplied by carbonatic raw materials such as dolomite and dolomite limestone, but may also by present in argillaceous materials. Crystalline MgO, in the form of periclase present in cement, tends to hydrate after setting, a condition which causes excessive expansion and possible disruption of concrete. For this reason, MgO is limited to 5 - 6 % in cement. However, the activity of periclase is also a function of the cooling rate of the cement clinker: slow cooling allows a large migration of ions and the subsequent development of large periclase crystals; rapid cooling results in an significant proportion of the MgO being frozen in various inactive solid solution.

SO_3

SO_3 is generally associated with gypsiferous carbonate sources or with pyrite-containing materials. SO_3 inhibits the volatilisation of the alkalis. It also requires - in form of SO_2 - special attention with respect to air pollution. Furthermore, SO_3 (as gypsum) above a certain optimum percentage causes a decrease in strength and an increase in expansion.

P_2O_5

P_2O_5 is mainly found in carbonate components. Contents of >1 % P_2O_5 in cement reduce the cement strength by raising the free lime content and combining with CaO in solid solution at the expense of the C_3S. Setting times are considerably affected as well.

Chloride (Cl)

Chloride is mainly supplied by sedimentary rocks containing or contaminated by salt. In wet preparation systems chloride attacks all metal installations; during burning it easily volatilizes and causes clogging and plugging in kilns and preheaters. Chloride in concrete jeopardises reinforcement by corroding.

Fluorine (F)

Fluorspar (CaF_2) was in the past added to many cement raw mixes as a fluxing agent. Although this material decreases the kiln reaction temperature, several undesirable effects - as deterioration of refractory lining in kilns, increase of dusting of the clinker through a tendency to convert β-C_2S to the γ-form, difficulties with setting times and a lowering of early strengths - led to a considerable reduction of consumption in the cement industry. Aside from those reasons, recent air pollution regulations prohibit the introduction of fluorides into the atmosphere.

Mn_2O_3

Manganese occurs normally as a constituent of corrective materials for iron deficiency. The presence of larger quantities (> 2 %) may lead to a dark coloured clinker.

Cr_2O_3

Chromium bearing cement may lead to the "chromium ekzema"; on the other hand it is apparently possible to improve the cement strength to a certain extent by adding Cr_2O_3 - bearing components to the raw mix ("doping of alite").

It is furthermore claimed that Cr_2O_3 could also affect the colour of cement.

TiO_2

Titanium reacts as fluxing agent decreasing the alite content and increasing the belite content in clinker. It produces a darker cement colour, increases strength and retards initial setting.

Tab. 39 summarises the influence of some minor components.

Table 39   Mineralogy of major deleterious constituents in cement raw materials.

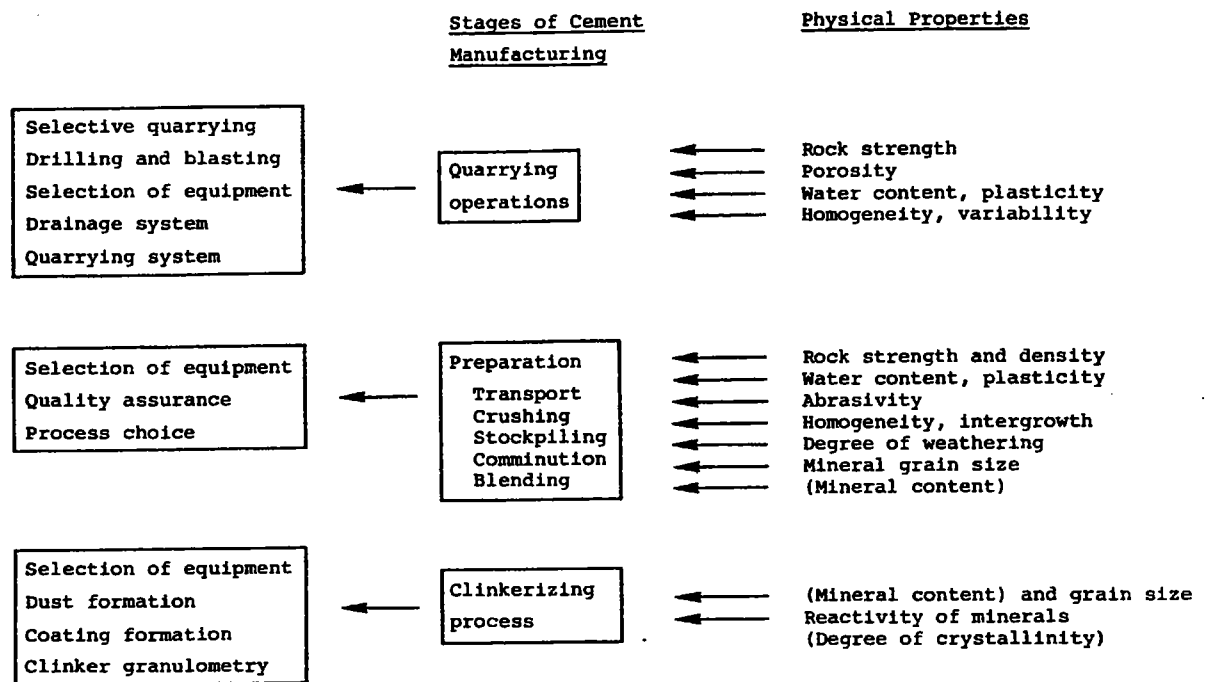|	$K_2O + Na_2O$		MgO		SO_3		P_2O_5		SiO_2
	Mineral	Alkali content	Mineral	MgO content	Mineral	SO_3 content	Mineral	P_2O_5 content	Mineral
	Feldspars		Dolomite	21.7 %	Gypsum	46.6 %	Collophane	15-40 %	Chert
	Albite	11.8 % Na_2O	Magnesite	47.6 %	Anhydrite	58.8 %	Apatite	41-42 %	Chalce-
	Oligoclase	8.3-10.6 % Na_2O	Periclase	100.0 %	Pyrite	53.4 %			dony
	Andesine	5.9- 8.3 % Na_2O	Brucite	69.0 %					Quartz
	Labradorite	3.5- 5.9 % Na_2O	Montmoril- lonite	2.5-6.5 %					Opal
	Microcline	16.9 % K_2O							
	Orthoclase	16.9 % K_2O	Chlorite	30-37 %					
	Mica - Illite		Amphiboles, proxenes, micas	15-30 %					
	Biotite	10.0-11.0 % K_2O							
	Muscovite	11.8 % K_2O							
	Illite	5.5 % K_2O							
Reason for deleterious effect	Causes deterioration in concrete when combined with reactive aggregate		Expansion caused hydration of MgO to brucite-$Mg(OH)_2$		Inhibits volatilization of alkalis		Decreases early strength through reduction of C_3S		Increased mining, milling, and fuel costs
Limit in cement	0.6 % $(Na_2O + .658 K_2O)$ for low-alkali cement		5.0 - 6.0 %		2.3 - 4.0 %		1.0 - 1.5 %		

1.4.3   Assessment of Physical Properties

1.4.3.1 General

The description of the relevant physical ("engineering") properties is given in 4.3.5. Basically, limits or guidelines for physical properties can hardly be given. In practice, appropriate process-technological methods have to be selected and adapted in order to permit optimum processing.

A series of physical properties and their effects on various stages of the cement manufacturing process are listed in Table 40. The influence of these properties is known only very generally; it is almost impossible to express them quantitatively, because only a few out of the total can be measured exactly.

Table 40   Stages of Cement Manufacturing.

	Stages of Cement Manufacturing	Physical Properties
Selective quarrying Drilling and blasting Selection of equipment Drainage system Quarrying system	Quarrying operations	Rock strength Porosity Water content, plasticity Homogeneity, variability
Selection of equipment Quality assurance Process choice	Preparation Transport Crushing Stockpiling Comminution Blending	Rock strength and density Water content, plasticity Abrasivity Homogeneity, intergrowth Degree of weathering Mineral grain size (Mineral content)
Selection of equipment Dust formation Coating formation Clinker granulometry	Clinkerizing process	(Mineral content) and grain size Reactivity of minerals (Degree of crystallinity)

1.4.3.2 Examples of Practical Experience

Quarrying operations

The content of "hard" minerals is important. Quartz being harder than steel has an abrasive influence, mainly on drilling equipment. In cases of large quartz content and high rock strength, drilling will progress slowly and abrasion will be high. Such a rock has a high "rock hardness".

The water content of the material to be quarried depends partially on the minerals present. Clay minerals, especially montmorillonite, mixed layers, illite, absorb large amounts of water. Clays thus have a high plasticity, they become adhesive, with more water slurry-like and dry very slowly. Clogging of machinery results, and quarry drainage becomes a problem.

Preparation

For crushing the rock strength has to be considered in the first place. It is rather the impact resistance than the compressive strength which is important. Rocks having a high quartz content and a high compressive strength may behave as brittle Materials during crushing, whereas clay minerals containing rocks sometimes are better characterised to be elastic and thus more difficult to crush.

As in all disintegration processes the formation of dust is a severe problem. This is especially the case when quartz, feldspar and micas are present in large amounts (e.g. in siliceous and related rocks), whereas the tendency of dust formation is much lower with clay bearing rocks. Quartz dust of a certain fineness ($<5\ \mu$) is the main cause of silicosis, a disease that attacks people working for longer periods in a dust environment (quarries, galleries, crusher buildings).

Again rock strength and mineral hardness play a determining role for grinding. In addition, the mineral grain size as compared to the raw meal fineness is influencing the grindability. Raw meal particles may either be mineral or rock fragments. It is assumed that coarser single minerals are disintegrated more easily, especially when the minerals have a good cleavage (e.g. calcite), than rock pieces consisting of different very finely grained and densely intergrown minerals. Quartz will contribute to the abrasion of the grinding equipment-, but can also take part in the disintegration of softer minerals. Thus a difference in mineral hardness can be an advantage.

Usually, the quartz content of coarser raw meal fractions is higher than in the fine fractions. This fact can be utilised in cases where a limestone with a too high quartz content, e.g. silex inclusions, has to be used.

Coating sometimes becomes a problem during grinding. Among many different reasons the properties of micas and clay minerals - flaky shape, water content, plasticity - possibly contribute to this problem. From experience it is known that coating also may appear when aragonite is present in the raw material instead of calcite.

For raw mix preparation, homogeneity and variability of the raw mix components are of paramount importance. Specific physical parameters become impotent when the most suitable process has to be selected. The wet process is considered when the raw Materials have a high water content. That can be especially the case in the presence of clay minerals such as montmorillonite and illite absorbing large amounts of water. The viscosity of a slurry depends strongly on the type of clay mineral present. If montmorillonite and other clay of high plasticity are predominant, much more water is needed to get a slurry of sufficient flow properties.

To produce nodules of sufficient strength for the Lepol process, plastic clay minerals have to be present. Raw meals containing mainly quartz, feldspar and mica are hardly nodulizable with a reasonable water content.

In the case of a dry kiln there are no severe restrictions to be mentioned in this stage of the process. The question is always how much energy will have to be needed for raw material drying.

The clinkering process

The reactivity of raw mix depends on the intensity of the contact between calcareous and siliceous components which have to react together. In an argillacecus limestone both components are tightly intergrown within the rock texture itself. If at the same time the mineral grain size is well below the average grain size of the raw real, each particle contains both components needed for reaction. This results in a high reactivity which is not greatly influenced by the raw meal fineness. If the calcareous and the siliceous components occur in different rocks or in coarse grained minerals, a much finer grinding and a very effective homogenisation are essential for a goad reactivity.

Water bearing clay minerals react more readily than water free silicates such as quartz, feldspar and mica, because their mineral lattices are already partially destroyed when the carbonate starts to dissociate at about 600 - 700°C and therefore in a more reactive condition.

Poorly crystallised clay minerals and gel-like hydroxides having a low degree of crystallinity have a higher reactivity than minerals with well defined crystal lattices. The same is true for amorphous SiO_2 (i.e. silex, opal) as compared with quartz.

The exact knowledge of the mineralogical raw mix composition shows in which form minor elements occur. Feldspar, mica and illite e.g. are the principal alkali bearing minerals. From an illite raw mix the alkalis evaporate at lower temperatures than from a mix rich in feldspar. Under certain conditions this fact should be considered in practice.

The tendency to form dust depends also on the mineralogy. Mixes with water free and well crystallised silicates tend to develop more dust than clay mineral containing mixes.

Jura Wildegg
Limestone Quarry

Drill-rig

Make	Hausherr HBM 12
Drive	Hydraulic
Feed rate (m/min)	0 - 6.0
Drilling rate (m/hr)	30.0
Bench height (m)	5.0 - 25.0
Burden (m)	3.6
Spacing	3.0

Drill bit - 2 stage	
Centre (mm)	65
Reamer (mm)	80

Mobile Crusher
Weserhütte

Apronfeeder

Apronfeeder - angle (°)	30
- width (m)	2.0
Installed Power (kW)	40
Velocity (m/s)	0.05 - 0.15

Mobile Crusher
Weserhütte

Double Shaft Hammer Crusher
Titan - Miag

Tonnes/hr nominal	500
Max feed size (mm)	1 500
Final product size (mm)	0 - 20
Grate size (mm)	25
Rotor dimensions (mm)	1 800 * 2 110
Installed power (kW)	2 * 400

Hammers	
Number / row	17
Number / rotor	34
Weight (kg)	90

Jura Wildegg Cement
Marl Crusher
Hazemag Compound

	Marly Limestone	Marl
Tonnes/hr	650	650
Product Size (mm)	0-30	0-70
Max Feed Size (mm)	1 500	1 500
Moisture content (%)	13-15	
RPM Rotor 1	370 (36m/s)	360 (26 m/s)
Rotor 2	480 (45 m/s)	330 (35 m/s)
Power Cons. kW/t	0.5	0.4

ASSESSMENT OF RAW MATERIALS

ASSESSEMENT OF RAW MATERIALS

CRITERIA

- chemical composition to conform cement requirement

- handling and comminution properties

- burning behaviour

DETERMINED BY

- chemical composition

- mineralogical composition

- petrographical properties

COMPARISON
CHEMICAL ELEMENT REQUIREMENT CEMENT
V.S.
OFFER EARTH CRUST

ELEMENT	TYPICAL FOR CEMENT (%)	AVERAGE CONC. EARTH CRUST (%)
Ca	46	4
Si	10	28
Al	3	8
Fe	3	5

CHEMICAL COMPOSITION

MAIN ELEMENTS	MINOR ELEMENTS	TRACE ELEMENTS
SiO2 (22%)	MgO	Tl
Al2O3 (5%)	SO3	Cd
Fe2O3 (4%)	K2O	Hg
CaO (64 %)	Na2O	etc
	TiO2	
	Cr2O3	
	Mn2O3	
	P2O5	
	Cl	
	F	
	etc	

(typical for OPC)

CLASSIFICATION OF CALCAREOUS COMPONENTS

CaCO3	Designation	Petrographic desig.
95–100	high grade limestone	limestone marble chalk coral limestone lime sand shell deposit
85–95	limestone	
75–85	marly limestone	marly limestone

CLASSIFICATION OF ARGILLACEOUS COMP.

CaCO3	Clay	Designation	Petr. design.
65–75	25–35	calcareous marl	calcareous marl
35–65	35–65	marl	marl
25–35	65–75	clayey marl	clayey marl
15–25	75–85	marly clay	clay loess
5–15	85–95	clay	claystone mudstone siltstone
0–5	95–100	high grade clay	shale

CORRECTIVE MATERIALS

TO CORRECT THE DEFICIENCY OF	CORRECTIVE MATERIAL	MINIMUM CONCENTRATION
"IRON" (Fe_2O_3)	IRON ORE PYRITES ASH	60 % Fe_2O_3 60 – 90 % Fe_2O_3
"ALUMINA" (Al_2O_3)	BAUXITE LATERITE KAOLINITE	50 % Al_2O_3 25 % Al_2O_3 40 % Al_2O_3
"SILICA" (SiO_2)	QUARTZSAND QUARTZITE	80 % SiO_2 80 % SiO_2
"LIME" (CaO)	LIMESTONE MARBLE	90 % $CaCO_3$

EFFECTS OF MINOR ELEMENTS

Element	Concentr. raw meals %	Limits cement %	Effect
MgO	0.50–4.0	5–6 norms	Expansion
SO3	0.04–1.06	2.3–4 norms	Volatilisation Setting behaviour Emission
K2O Na2O	0.01–1.40 0.03–0.60	0.8 low alk.	Volatilisation Alkali aggregate reaction

EFFECTS OF MINOR ELEMENTS

Element	Concentr. raw meals %	Limits cement %	Effect
P2O5	0.03–0.50	appr. 1.0	reduces strength
Cl	0.01–0.2	0.05–0.1 in several norms	volatilisation corrosion
F	0.00–0.24		flux problematic setting strength reduction emission

EFFECTS OF MINOR ELEMENTS

Element	Concentr. raw meals *	Limits cement *	Effect
TiO_2	0.10–0.47		flux retards init. setting increases strength
Cr_2O_3	0.01–0.05		"chromium ekzema" colour
Mn_2O_3	0.03–0.83		colour
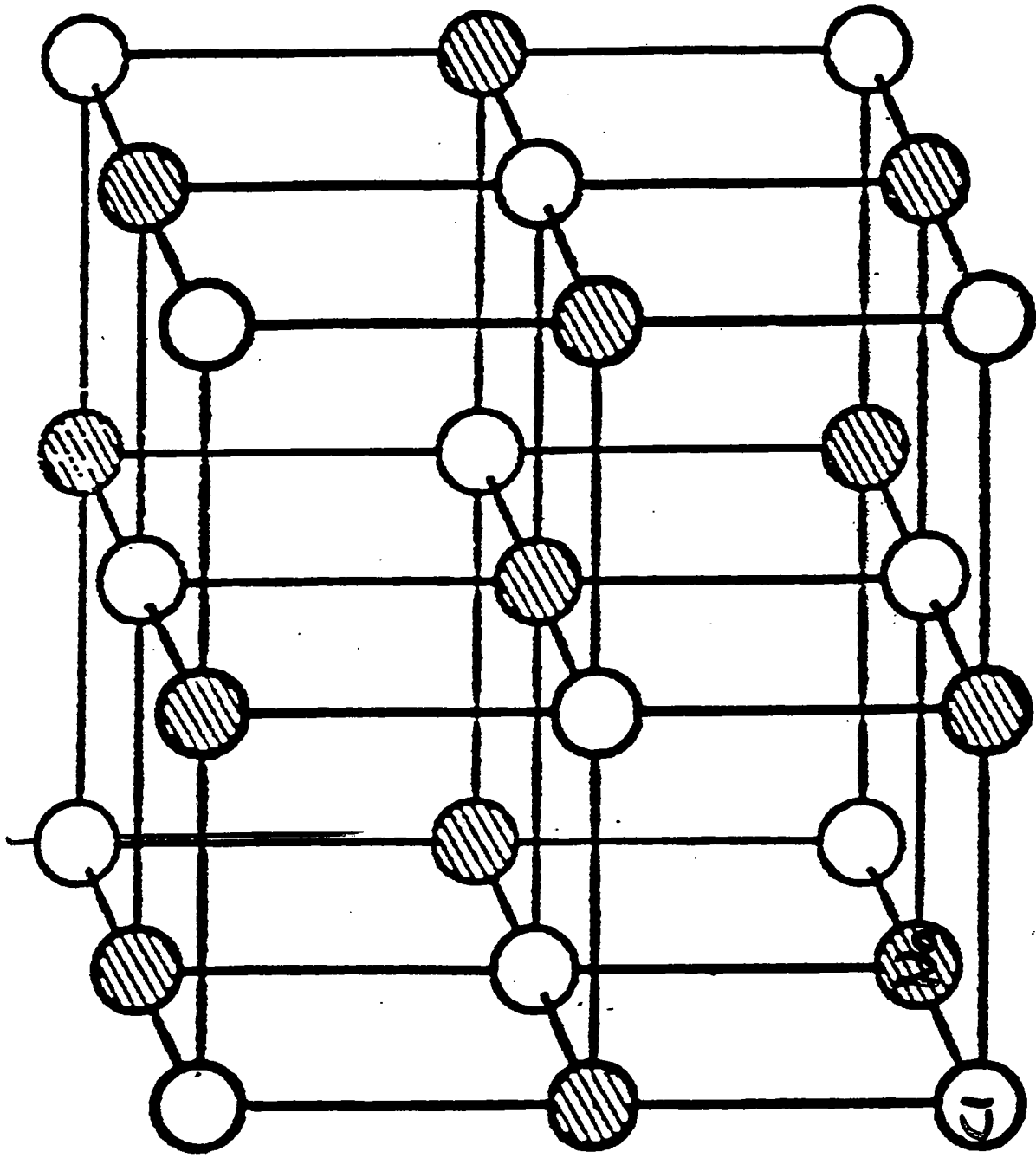
*Bild 19. Die Elementarzelle (Würfel)
der Steinsalzstruktur*

MINERALOGICAL COMPOSITION OF RAW MIXES

CARBONATES

- calcite — $CaCO_3$
- aragonite — $CaCO_3$
- dolomite — $CaMg(CO_3)_2$
- magnesite — $MgCO_3$
- siderite — $FeCO_3$

SILICATES

- quartz — SiO_2
- feldspars — eg. $(K,Na)AlSi_3O_8$
- micas
- clay minerals
- amphiboles
- pyroxenes
- olivines

TYPES OF LINKAGE OF
SiO$_4$ - TETRAHEDRA

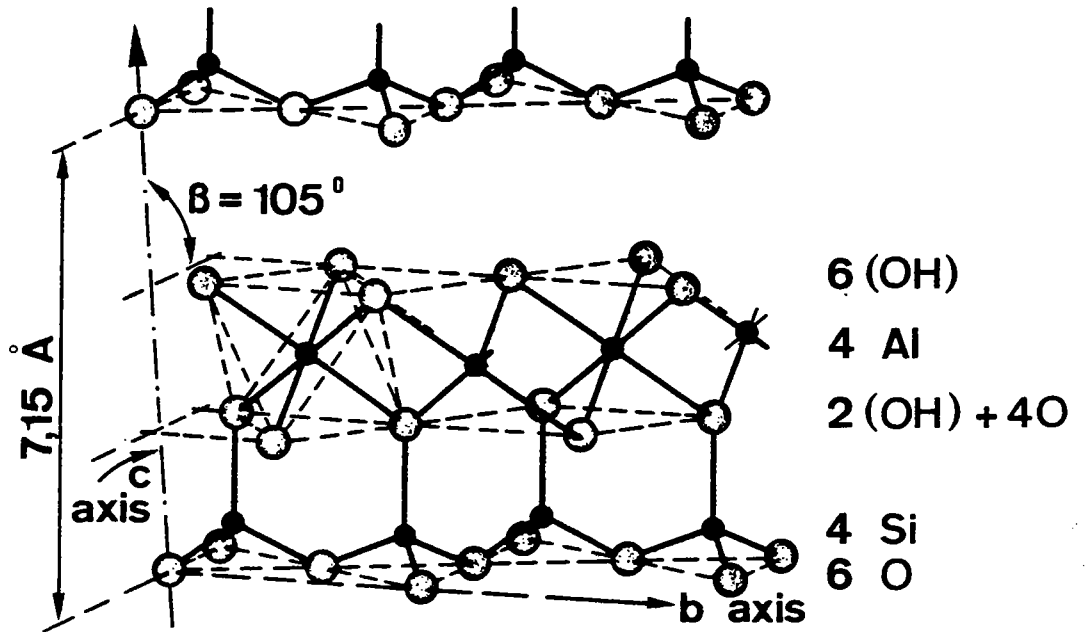## SiO$_2$
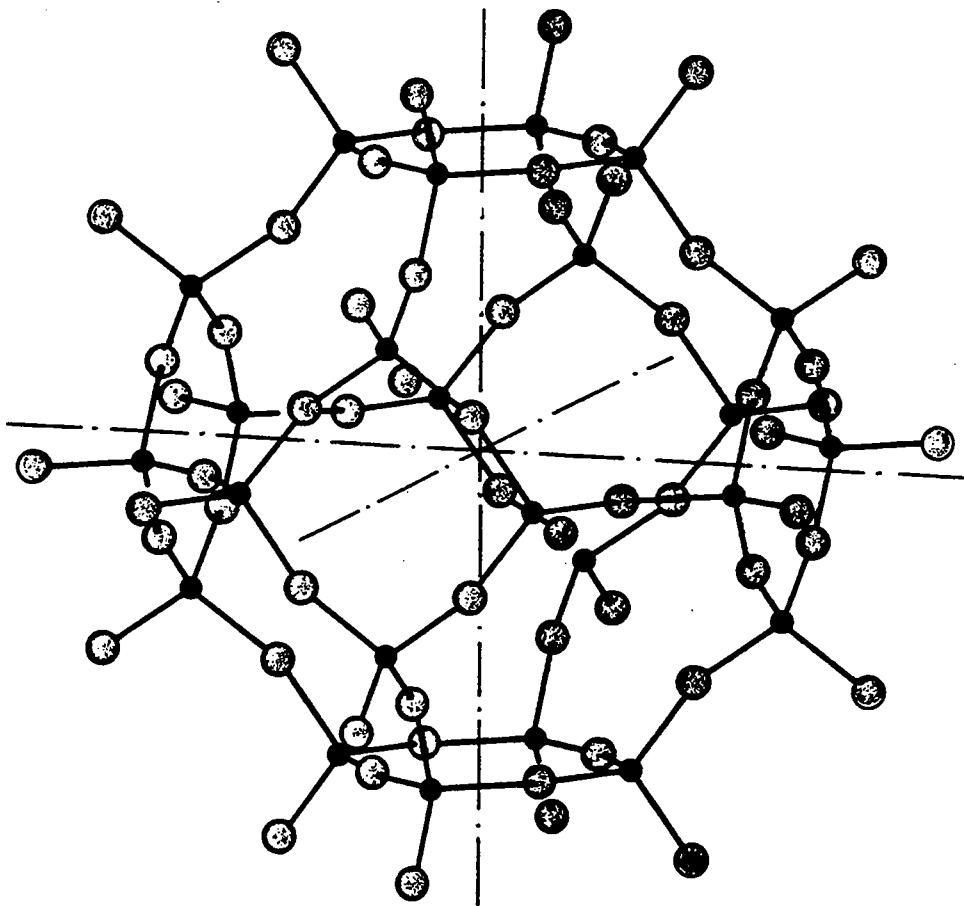
THREE DIMENSIONAL FRAMEWORK

Ångström units

0 1 2 3

Table 34 : Hardness of most abundant minerals according to Mohs

Mineral	Mohs scale	Valuation
Quartz	7	"hard" minerals
Feldspar	6	
Pyroxene	6	
Amphibole	6	
Calcite	3	"soft" minerals
Dolomite	3.5	
Mica	3	
Chlorite	2 - 3	
Clay minerals	2	

Fig. 48

CLAY MINERAL STRUCTURES

$\beta = 105^{0}$

7,15 Å

c axis

6 (OH)

4 Al

2 (OH) + 4O

4 Si

6 O

b axis

TWO-LAYER STRUCTURE (KAOLINITE)

14,3 Å

c axis

6 O

3 Si + 1Al

2 (OH) + 4O

5 Mg + 1Al

2 (OH) + 4O

3 Si + 1Al

6 O

b axis
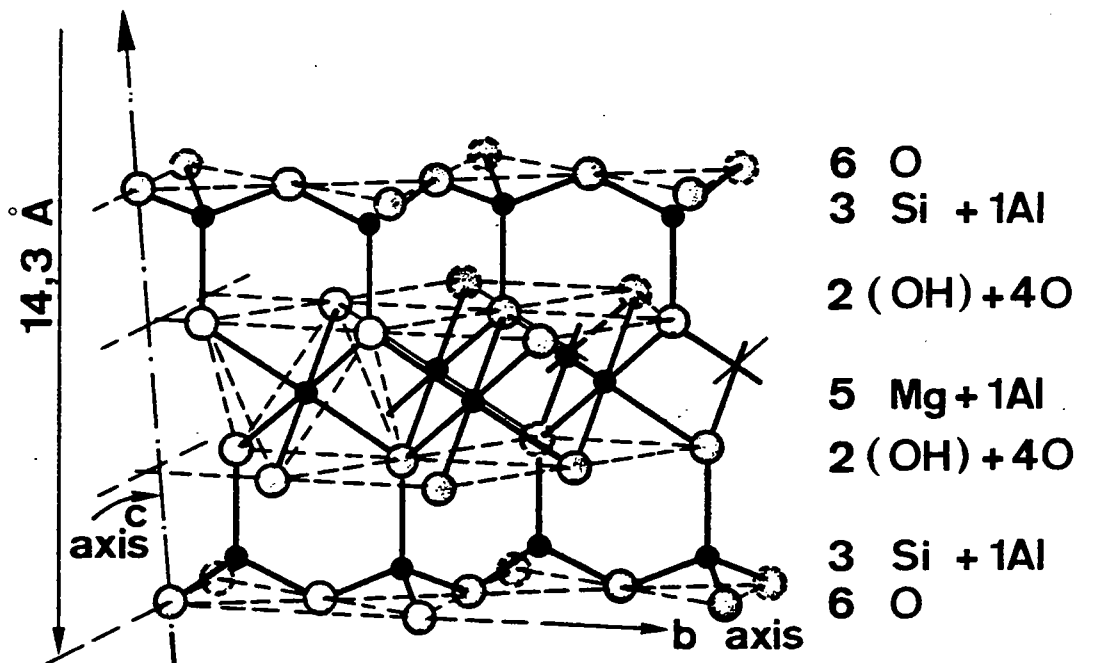
THREE-LAYER STRUCTURE (CHLORITE)

ROCK CHARACTERISTICS

. mineral assemblage : types of minerals present

. texture and structure

     – spacial distribution of minerals

     – form of minerals

     – size distribution of minerals and pores

     – orientation of minerals and pores

. consolidation

PHYSICAL ROCK PROPERTIES

. density and porosity

. water absorption, moisture

. compressive strength

. elasticity

. cleavability
. hardness
. crushability

. abrasivity
. grindability

Table 32   Density and porosity of rocks

Rock	Specific gravity (density) g/cm^3	Porosity %
Granite	2.5 - 2.8	0.5 - 1.5
Diorite	2.6 - 2.9	0.1 - 0.5
Gabbro	3.0 - 3.1	0.1 - 0.2
Dolerite	3.0 - 3.1	0.1 - 0.5
Rhyolithe	2.4 - 2.6	4 - 6
Andesite	2.2 - 2.3	10 - 15
Basalt	2.8 - 2.9	0.1 - 0.2
Tuff	2.8 - 3.0	high
Sand (loose)	1.5 - 2.0	25 - 50
Sandstone (compacted)	2.0 - 2.6	10 - 30
Shale	2.0 - 2.4	10 - 30
Limestone	2.2 - 2.6	5 - 20
Dolomite	2.5 - 2.6	1 - 5
Marl	1.6 - 2.6	5 - 30
Clay	1.5 - 1.9	30 - 50
Claystone	1.8 - 2.3	15 - 35
Gneiss	2.9 - 3.0	0.5 - 1.5
Marble	2.6 - 2.7	0.5 - 2
Quartzite	2.6 - 2.7	0.1 - 0.5
Slate	2.6 - 2.7	0.1 - 0.5

Table 33   Compressive strength of rocks

Rock type	Compressive strength kg/cm² / N/mm²		Valuation (of compressive strength)
Basalt Quartzite	>2800	/ >280	very high
Granite Diorite Limestone	1800 - 2800	/180 - 280	high
Sandstone Limestone Marble Slate	800 - 1800	/ 80 - 180	medium
Porous lime-stone	400 - 800	/ 40 - 80	low
Chalk, Tuff, Shale, Clay, Claystone	<400	<40	very low

GRINDABILITY OF RAW MIXES

"Holderbank" Grindability Test; 10 % Residue on 90 μm)

	A	B	C
GRINDABILITY KWH/T	12	17.5	22
ASSESSED AS	GOOD	MEDIUM TO POOR	VERY POOR
COMPONENTS	85.7 % LIMESTONE	87.2 % LIMESTONE	77.7 % LIMESTONE
	MARLY LIMESTONE	LIMESTONE	HIGH GRADE LIMESTONE
	POROUS, FINE GRAINED, HOMOGENEOUS	RECRYSTALLIZED, DENSE, HARD	
	14.3 % CLAY	12.8 % CLAY	16.5 % SHALE
			5.7 % SANDSTONE